Groundwater Treatment by Electrodialysis: Gearing Up Towards Green Technology

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Abstract

Experiments on electrodialysis stack to treat groundwater was conducted and evaluated. The stack was operated at optimum experimental conditions at applied voltage of 12V, feed flow velocity of 0.033 l/s and desalination time of 92 minutes. An average cation removal efficiency of 99.15% was obtained while 100% anion removal was recorded for the all the anions except Cl with 99.97% removal efficiency. The oxidation-reduction potential (ORP) was also recorded to increase from -162.2 mV 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. Solution pH was also noted to drop from 7.62 to 4.80 with corresponding decrease in the conductivity of 1388 µS/cm to 36 µS/cm. This indicates that characteristics of product water can be classified that of purified water, suitable for drinking and analytical purposes when process was controlled for such purpose. Arsenic desalination kinetics was found to increase over time at constant applied voltage and feed flow rate with corresponding decrease in current utilization. Lower As feed concentration samples tend to achieve product water concentrations of lower than MCL of 10 ppb earlier than high feed concentration samples.

Keywords: ED, Electrodialysis, groundwater treatment, remediation, green technology

1. Introduction

One of the basic rights of the people is the access to safe drinking water. Several guidelines for drinking water quality was developed and amended since the 1900s stressing on the importance of water sanitation and hygiene for health. In 2006, the United Nations General Assembly declared the periods 2005-2015 as the International Decade for Action, "Water for Life" (WHO, 2006). In the first addendum to the 3rd edition of the Guidelines for Drinking Water Quality, three (3) important qualities are suggested to be monitored strictly, namely microbial, chemical and radiological characteristics of drinking water. Surface and groundwater are the two (2) 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 has resulted in greater demand on the quantity of drinking water, leading to catastrophic water shortage in several areas of the world. With the fact that only around 0.8% of the total earth's water is fresh water (Greenlee *et al*., 2009), groundwater resources are being exploited to meet the demands of the various sectors (Annapoorna and Janardhana, 2015). It is projected that by year 2030, the global needs of water would increase to 6900 billion m^3 from the current 4500 billion m^3 (Misdan *et al*., 2011). So, 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 ground waters were mostly polluted due to natural phenomena and anthropogenic activities of man. The contamination of groundwater with metals is primarily attributed to anthropogenic activities, which requires risk assessment to characterize the nature of magnitude of the threats to humans and ecological receptors (The *et al*., 2016). Urban development also limits the permeability of ground surfaces such as: precipitations that would not normally reach natural land and surface infiltrates into the underlying aquifer (Maloney *et al*., 2014; Rusu *et al*., 2012) and the natural migration of the trace elements in the soils due to soil and rock weathering into the groundwater. 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 (USEPA, 2006). Over the years, electromembrane techniques are being employed to treat and remediate groundwater for drinking purposes. Electrodialysis (ED) is an electrically-driven membrane process used in the separation of ions across charged membrane from one solution to another has been documented to be an efficient technology in removing chemical contaminants from industrial waste water (Chandramowleeswaran and Palanivelu, 2006; Mendoza,

2013). Though ED's dominant application is still in desalination, ED becomes an attractive alternative to the traditional groundwater treatment and remediation. With the onset global spiralization to climate change and environmental sustainability, scientist and researchers are being directed to the application of science and technology for the development of process, products, equipment and systems that conserved natural resources and environment or what is popularly known as green technology (Bhowmik and Dahekar, 2014). In the field of drinking water production, this means having a treatment or remediation process that produces lesser or zero (0) by-products that poses threat to the environment. This study evaluated the performance of electrodialysis (ED) as a treatment process for contaminated groundwater and its potentials in providing potable drinking water, in a cleaner, more environmentally sustainable manner.

2. Experimental

Groundwater samples used in this experiment were obtained from raw water source, well no. 9 and 10 of Taiwan Water Corporation's Water Treatment Plant in Beigang Township, Yunlin, Taiwan. Characteristics of the groundwater used for this study was presented in Table 1.Groundwater protocol on preservation and arsenic speciation procedures are the same as that of Bednar *et al*. (2004).

Table 1. Physical and Characteristics of the Sample Ground water used in this study

Cations	Concentration (ppb)	Anions	Concentration (ppb)
Na^{+}	145.50	Cl^{-}	130.60
K^{+}	34.52	NO_3^{-}	<0.10
Mg^{2+}	18.97	HCO_3^{-}	119.70
Ca^{2+}	20.75	SO_4^{2-}	2.29
Mn^{2+}	0.09	PO_4^{3-}	6.30
Fe^{tot}	<0.01	TOC	1.19 mg C
As^{tot}	232		

E_h= -162.2 mV; pH=7.68; T=23°C; EC=1388µS/cm

The experimental methods for this study was the same as the experimental procedures of Mendoza *et al*. (2014). Cation concentrations (Na, Mg, Ca, K, Mn and Fe) of the feed, diluate stream and concentrate stream was 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, sulphates 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.

3. Results and Discussion

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 terms of the cations present in the groundwater sample, an average removal efficiency of higher than 50% was achieved in the first 5 minutes of desalination. Figures 1A and 1B indicates that the removal of cations and anions in the groundwater is primarily affected by the desalting or operating time. Na^{+} and K^{+} exhibits almost the same desalination pattern which is also the same trend as the desalination pattern of Ca^{2+}, Mg^{2+} and Mn^{2+}.

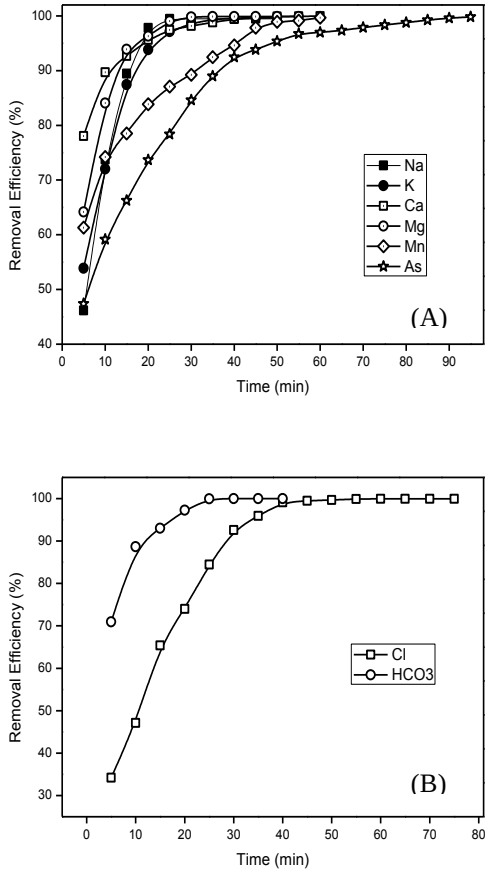

Figure 1. Removal efficiencies (in percentage) by Electrodialysis with respect to time of (A) Cations, and (B) Anions present in the sample groundwater.

Arsenic which is of 2 species (As^{+5} and As^{+3}) resembles the pattern of the first two groups, but of a lower removal rate. Desalination time required to achieve more than 99.5% removal for ach cations vary, with cations having +1 charge desalts faster than that of divalent cations and Arsenic with charges +5 and +3 desalts longest. For the anions, the ED process was found to exhibit a more superior performance than cation removal. This is due to the fact that majority of the anions (NO_3^{-}, SO_4^{-} and PO_4^{-}) were removed in the first 5 minutes of desalting time. Extending the desalting or operating time to several more minutes removed 100% of HCO_3^{-} and 99.9% of Cl^{-}. In general, both cation and anion removal from the sample groundwater was achieved in less than 100 minutes of desalting time.

3.2. Diluate and Concentrate Streams

The basic ED mechanism results in two product flow regimes, the diluate stream which is characteristically clean water and concentrate stream which is the enriched or dirty water. The depletion of cations was achieved in the diluate stream and enrichment of cations achieved in the concentrate stream is illustrated in Figure 2A and 2B. Chemical analysis of the diluate and concentrate streams manifest a considerable reduction of cations and anions as compared to the initial sample concentration. Cationic and anionic concentrations with respect to operating time phenomenally decreased from 5 to 20 minutes of desalting time. Desalination becomes marginal after 30 minutes onwards, 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 (Mendoza *et al*., 2014). 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.

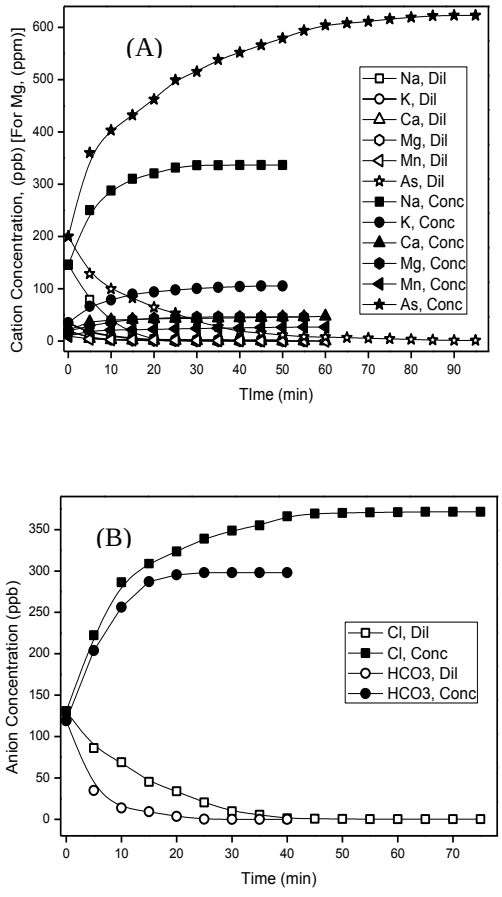

Figure 2. Product water concentrations of the Electrodialysis of sample groundwater. (A) Cation concentration and (B) Anion Concentration. (Dil = Diluate Strean, Conc=Concentrate Stream)

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 basically reduces the ability of the solution to carry electrical current due to lower electrical conductivity.

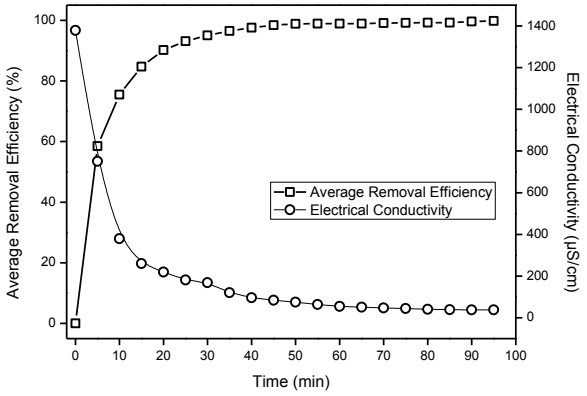

Figure 3. Electrical conductivity and removal efficiency with respect to time of the Electrodialysis of groundwater.

3.3. Arsenic Desalination Kinetics

Of the cations present in the sample groundwater, Arsenic is the most harmful. The presence of arsenic particularly in drinking water poses a very tremendous threat to human health. 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 to the 10 ppb Maximum Contaminant Level (MCL) mandated by USEPA and WHO (WHO, 2004; USEPA, 2006). From Figure 4, the increased desalination of arsenic with its operating time is due to the fact that the prolonged removal or separation of Arsenic from ground water samples is due to its interaction with the other cations and anions affecting the kinetics and the thermodynamics of ED, while the decrease in the current utilization with respect to operating time is brought by the removal of transporting ions that generates current in the system. As the operating time approaches optimum which is at 95 min (Mendoza *et al*., 2014), the current utilization was observed to approach a constant value, which signifies the depletion of ions in the boundary layer, but not polarization. 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 (Tanaka, 2010). This means that the system is operated way below the concentration polarization region which indicates current utilization efficiency.

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 ground water sample from its original state, 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 pure water and purified water physical characteristics. It was observed that product diluate stresm produced by

eletrodialysis competes with that of purified water, again indicating te huge potential of ED to make potable drinking water.

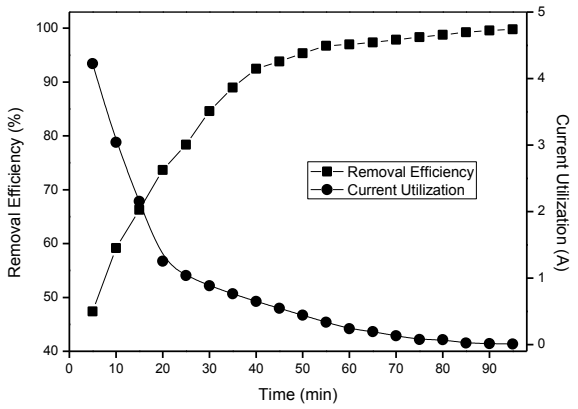

Figure 4. Product water desalination and current utilization kinetics of the electrodialysis of sample groundwater.

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[c]
Mg^{2+}	<0.01	HCO_3^-	ND[c]
Ca^{2+}	0.01	SO_4^{2-}	ND[c]
Mn^{2+}	ND	PO_4^{3-}	ND[c]
Fe^{tot}	ND	TOC	ND[c]
As^{tot}	0.88		

E_h= 908 mV; pH=4.80; T=25°C; EC=36µS/cm

[c]ND = none detected

The very high pH of the product diluate stream further attests to its purity. This is because high purity waters rapidly pick up contaminants like CO_2 from air, which affects its low conductivity and pH. Which 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 definitely still in high purity (Pro-Analitika KFT, 2015). In addition, the collecting tanks for the diluate stream is uncovered which might facilitate atmospheric CO_2 adsorption, on top of the carry-over of contaminant due to the recirculation process. The oxidation-reduction potential (ORP) was also recorded to increase from -162.2 mV 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, thus, making the clean product water also an excellent solvent for analytical and laboratory preparations. The concentrate stream, on the other hand of this ED process, with its very high ionic concentrations can be reprocesses for ion/salt recovery for commercial and even pharmaceutical utilization. For instance, the very high concentration of arsenic which is around 600 ppb (from Figure 2A) 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 (Bian *et al*, 2012) approved by the USA FDA as Trisenox in 2000, while calcium magnesium and manganese derivatives also share the same fate.

Table 3. Comparison of the Physical Characteristics of Pure Water, Purified Water and the Product Water (diluate stream) of this study

Parameters*	Pure Water[a]	Purified Water[a]	Product Water (This Study)
EC (µS/cm)	0.2 – 1.0	1 - 50	36
ER[b] (MΩ·cm)	1-10	0.02 – 1.0	0.034
pH	7.0	6.6- 7.6	4.8
TDS (ppb)	-	1.4	1.02

* Measured at T = 25°C

[a]Source: Pro-Analitika KFT, Hungary (2015)

[b]Electrical Resistivity

4. Conclusions

The process of producing potable drinking water from treatment and remediation of ground water by Electrodialysis (ED) has been evaluated. The product diluate stream's physical and chemical characteristics was observed to be between that of high purity water (pure) and purified water. With proper process control and optimization, two possible beneficial use of the product water is at hand; (1) the production of potable, 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 for the production of some significant pharmaceutical substances such as arsenic trioxide or Trisenox. Thus, the ED process sustainability goes a long way down to its potential to be a zero-waste process. A process now popularly called green technology, focused on the development of process that poses lesser threat to the environment.

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