

ELECTRO DIALYSIS FOR THE DESALINATION OF BACKWATERS IN KERALA

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ABSTRACT

With the declining freshwater source and increase in demand for the potable water need of desalination have increased. The electro dialysis can be put as an economic substitute for the desalination of the brackish water. This paper deals with the assessment of the effect contaminants in the desalination of natural brackish water using electro dialysis. The contaminants studied were Boron, Sulfate and Magnesium in the presence of chloride. The study was based on the function of pH at a constant voltage of 11 V. Magnesium, Chloride, and Sulfate was not affected by the pH variations and was removed to an efficiency of 94%, 95%, and 74% respectively. But the boron was not removed in neutral pH and showed a removal efficiency of 41% at pH 10 in an hour. There was significant interference in the removal of the Chloride ion and Sulfate ion.

KEYWORDS

Desalination, brackish water, Limiting Current Density, Fate of the contaminants, Concentration

1. INTRODUCTION

Many areas in the coastal region face acute water scarcity even though they are bounded by large water bodies. The inland water bodies near to the coastline region, normally known by the name backwaters, carry plenty of water with better quality than sea water. These water sources are not effectively utilized, as the quality of water being brackish. This urges the need for an economic desalination technology to provide the potable water to the community. Electro dialysis has proved to be an efficient desalination technology for the purification of brackish water when compared to other established technologies used in the desalination of sea water like distillation, reverse osmosis etc[1]. The main advantages of electro dialysis when compared to reverse osmosis are:

- Water recovery rates are high even in the presence of higher sulfate concentration,
- Due to higher mechanical and chemical stability the membranes life is high,
- Can be operated up to a temperature of 50°C,
- Membrane scaling and fouling is reduced due to process reversal,
- Lesser pre-treatment is required,
- Membranes have high tolerance level for chlorine and higher pH

The technology of desalination using electro dialysis encounter problems with the contaminant ions present in water and result in the reduction of the product water quality. The characteristics of ions, interference of ions, mobility, concentration and speciation, pH, flow rate etc influence the rate of removal of these ions. This in turn lead to higher operating cost and in the worst case may lead to the discarding of the technology. Thus the removal characteristics of various

contaminants should be studied. The experiments, to find the characteristics of the ions, were executed with the solution prepared in the lab with the ions equivalent to the concentration that found prevailing in the backwaters of the study area. The electro dialysis unit was operated in the optimum operation condition to study the characteristics of the contaminant ion through electro dialysis.

Thus the experimental investigations were divided into three stages 1) The identification of the contaminants that prevail in the backwaters of the study area, 2) Optimisation of the ED unit to be operated and finally 3) The fate of the selected contaminants through the electro dialysis unit

2. EXPERIMENT

2.1 Location

The backwaters of Kadamakuddy, 10.0652° N and 76.2451° E, a small village in Kerala, India, known for its Pokkali farming, was chosen as the site for the desalination experiments. The place was chosen because of the serious drinking water scarcity even though it was surrounded by large backwater bodies. The water quality of the available backwater sources were brackish in nature and thus could not be used directly. The scarcity reached its peak in the summer. There is a seasonal farming of shrimps (prawns) and the pokkali rice cultivation. The rice is cultivated in the offset of monsoon and the shrimp farming was done in the summer time. The water from the backwaters were utilised for the farming purpose as the water is available in abundant.

2.2 The Sample Analysis for the Critical Contaminants

As the water scarcity reaches its peak in summer the samples were taken during the peak summer time (March) for the analysis. The samples were analysed for the parameters of Salinity, Hardness, Total Dissolved Solids, Conductivity, Calcium Hardness, Sulfate, Nitrate, Heavy metals (Cd, Fe, Mn, Ni, Pb, Cr, Cu, and Zn), Boron, COD, and pH. The Boron, Chloride, Hardness, Calcium Hardness was found out by their respective titration method. Sulfate was analysed using the turbidity analysis with barium chloride. The heavy metals were found out by AAS. Fluoride was analysed with electrical potentiometer. pH, conductivity, dissolved solids were found out using the water quality analyser (Erico pvt limited)

2.3 Electro dialysis Unit Used

The electro dialysis used in the experiment is of type EDL57 and stacks of type ES57. The spacers used were silicon spacers with pore size 500 µm and is lined with silicon. The unit comprises of different components, the stack, 3 peristaltic pump, a flow meter, a power supply unit and 3 containers for the diluate, concentrate, and electrode rinsing solution respectively. The Centrepiece of the ED-Unit is the Membrane Stack on top of the laboratory plant. Inside the Membrane Stack there are two electrodes (anionic and cationic) and altogether 21 membranes (11 cationic membranes and 10 anionic membranes), separated through the spacers with a silicon lining.



Figure 1 The front (i) and the rear view (ii) of the electrodiagnosis unit

The membranes used were AMX and CMX type from NEOSEPTA Supplied by Tokuyama Soda, Japan.

Table 1: The characteristics of the membrane used

Parameters	Cation Exchange Membrane CMX	Anion Exchange Membrane AMX
Type	Strong Acid (Na type)	Strong Base (Cl type)
Characteristics	High mechanical strength	High mechanical strength
Electrical Resistance (ohm-cm ²)	3	2.4
Burst Strength(M pa)	>= 4	>= 2.5
Thickness (mm)	0.17	0.14
Temperature (°C)	<= 40	<=40
pH	0-10	0-8

2.4 The Optimisation of the Operational Parameters of the Unit

The major affecting operational parameter is the flow rate through the diluate and concentrate cell, as the flow rate determines the Concentration Polarization and the limiting current density of the unit at a particular velocity [2]. The voltage applied beyond the voltage of the limiting current density lost in the dissociation of water molecules. With the increase inflow rate, the Limiting Current Density (LCD) and the limiting voltage will be increased [3][4].Therefore it is necessary to find the limiting current density of the unit.

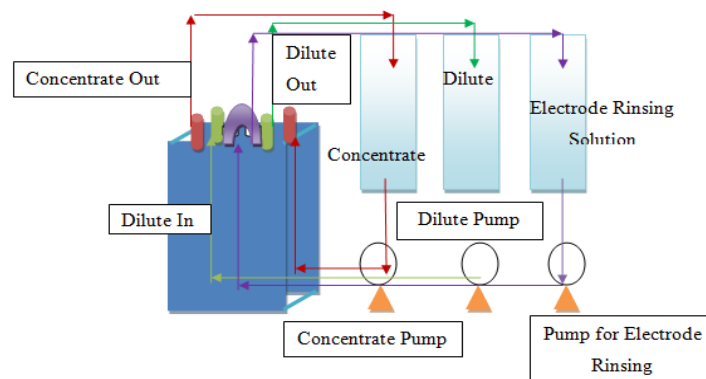


Figure 2 the schematic diagram of the experimental setup

Figure 2 shows the schematic diagram of the experimental setup. The optimisation of the flow velocity was done using a solution of sodium chloride of concentration (8g/l) and the limiting current density was found to a combination of different flow velocities of 20 % (34ml/min), 50% (85 ml/min), 80% (136 ml/min), 100% (170ml/min) in the diluate cell and 20%(34ml/min), 50%(85ml/min) and 100% (170ml/min) in the concentrate.

The procedure to find the limiting current density was.

- 1.) The tank was filled with the required concentration of synthetically prepared saline water.
- 2.) Created the limiting current density mode by placing the inlet and outlet pipe lines of the diluate and concentrate of the stack to a single tank (Figure 3). This will ensure the constant supply of the solution with the same concentration to concentrate and diluate cells in the stack. The diluate and concentrate pump must run for a short while to ensure complete and thorough mixing.)

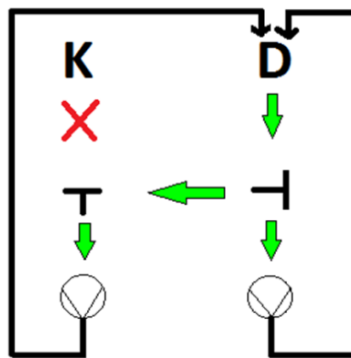


Figure 3 the water-flow circuit diagram for the analysis of the limiting current density

- 3.) The flow rate of the diluate cell was adjusted to the different percentages of maximum flow rate value (20%, 50%, 80%, and 100%). The flow rate at concentrate cell was also changed to various flow rates to check any influence on the Limiting Current Density (20%, 50%, and 100%)
- 4.) The control knob was adjusted to change the voltages starting from 0 V and increased to higher voltages with an increment of 2V. Then the electric current arises according to the stack resistance and it was measured from the ammeter.
- 5.) The limiting current density was determined graphically according to the Cowen and Brown method for the corresponding diluate volumetric flow rates.
- 6.) The experiment was repeated for the different flow rate of diluate and concentrate.

2.5 The Study on the Fate of the Contaminants in Electrodialysis

From the results of quality analysis conducted for water sample from Kadamakuddy, the critical contaminants were identified. The critical contaminants identified were chloride, hardness, sulphate and Boron. To study the removal efficiency of these contaminant ions, synthetic were prepared in the lab, to the same concentration as it was found in the backwaters, and were passed through the electrodialysis unit. The removal efficiency was evaluated for individual contaminants separately and different possible combinations of different contaminants. The electrodialysis unit was operated continuously for a time period of 1 hour each sample.

Since Boron changes its form in water according to the pH (in alkaline range), experimentation was repeated for different pH ranges. The pH adjustment was done using the 0.1 N NaOH. The unit was rinsed each time before every analysis to avoid any error in the concentrations and compositions.

3 RESULTS AND DISCUSSION

3.1 The Water Quality Data

The water quality data of summer are as given below. The chloride was found up to a concentration of 8g/l and a very high level of magnesium hardness to a concentration of 2.47g/l was found. The ions concentrations are expected to reduce in the monsoon due to the flushing of the more pure water from the tributaries. The sulfate was higher to 1.5 g/l but lower than the sea level concentration. The concentration of boron was also on a higher range (8mg/l). Thus the contaminants chosen were Boron, Sulphate and Magnesium as these were found to be more than the limit. The further experiments were continued with the water quality as in the summer.

Table 2. The water quality analysis data

Parameter	Concentration	Limit
pH	7.08	6.5-8.5
Chloride (mg/l)	8247	250
Total Hardness (as CaCO ₃) (mg/l)	2812	300
Ca Hardness (as CaCO ₃) (mg/l)	440	
Mg Hardness (as CaCO ₃) (mg/l)	2472	
Alkalinity mg/l	100	200
Calcium (mg/l)	176	75
Sulfate (mg/l)	1560	200
Total dissolved solids (g/l)	11.35	0.5
Boron (mg/l)	7.89	1
Iron (mg/l)	0.178	0.3
Fluoride (mg/l)	0.330	Should be b/w 0.6-1.5
Copper	ND	0.02 mg/l
Zinc	ND	5 mg/l
Chromium	0.035	0.03 mg/l
Manganese	0.115	0.1 mg/l
Cadmium	0.003	0.01 mg/l
Lead	ND	0.1 mg/l
Nickel	ND	0.05 mg/l

3.2 The Optimisation of the Electrodialysis Unit

After the identification of the contaminants the electrodialysis unit was optimised to find the maximum limiting current density.

Table 3: The analysis results of the optimisation of the operational parameters

Flow rate in Diluate(%)	Flowrate in Concentrate(%)	Limiting Current Density (A/cm ²)	Limiting voltage V
20	20	0.007943	8.19 V
	50	0.00818	8.28 V
	100	0.00810	8.25 V
50	20	0.0158	10.50 V
	50	0.0156	10.87 V
	100	0.0164	10.37 V
80	20	0.0229	13.84 V
	50	0.0223	13.31 V
	100	0.0238	13.56 V
100	20	0.0251	14.33 V
	50	0.0246	14.10 V
	100	0.0248	14.16 V

From the analysis a flow rate of 100% in diluate and 50% in concentrate was chosen for the further analysis. Voltage corresponding to the 80 % of the limiting current density was fixed for the further analysis which was 11V. The 80 % of the limiting current density was chosen to ensure the unit is run at a safer voltage. The limiting current density/ the limiting voltage were found by plotting the Cowen- Brown Method. The plot is as showed below,

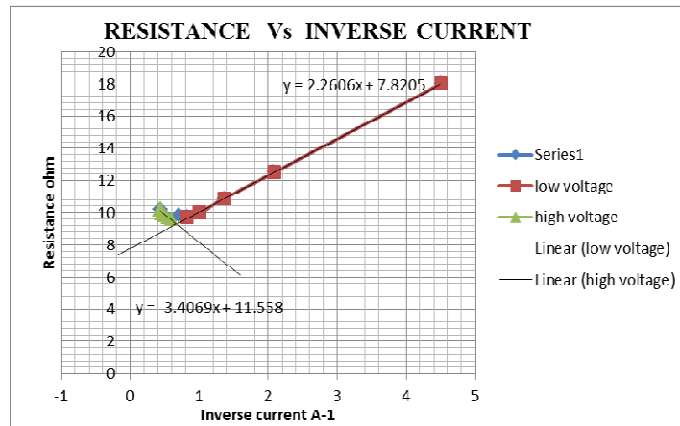


Figure 4 The Cowen – Brown curve of the analysis of the limiting voltage.

Calculation for the limiting Voltage from the Cowen –Brown Plot:

$$y = 2.2606x + 7.8205 \text{ (from the graph)}$$

$$y = -3.4069x + 11.558 \text{ (from the graph)}$$

Solving both the equations,

$$x = \text{inverse current (1/A)} = 0.659 \text{ A}$$

$$\text{Current} = 1/0.659 = 1.517 \text{ A and}$$

$$y = \text{resistance (Ohm)} = 9.311 \text{ Ohms}$$

By ohms law,

$$\text{Voltage } V = \text{Current (I)} \times \text{Resistance (R)}$$

$$\text{Voltage} = 1.517 \times 9.311 = 14.128 \text{ V}$$

$$\text{Area of the spacers} = 14.6 \text{ cm} \times 4.2 \text{ cm}$$

$$\text{Limiting current density} = 1.517 / (14.6 \times 4.2) = 0.02473 \text{ A/ cm}^2$$

3.3 The Fate of the Identified Contaminants

After the operational parameters were fixed, the analysis of the contaminants was begun. The contaminants chosen were Boron, Sulfate, and Magnesium. The solutions were synthetically prepared to the concentration of that particular ion.

3.2.1 Fate of Chloride

Chloride, the basic component of salinity was analysed first to set a baseline. The concentration of chloride taken was 8g/l as per the analysis results of the backwater in summer. The diluate chamber and the concentrate chamber were filled with 1 litre solution of chloride of concentration 8g/l respectively. The pH was set to 7 as it was found in the site conditions. The electro dialysis unit was operated for an hour and samples were taken from the diluate as well as the concentrate chamber on every 10 minutes time interval. These samples were analysed to find the removal efficiency and the fate of the contaminants that were removed from the diluate container. The analysis was done with Argentometric method.

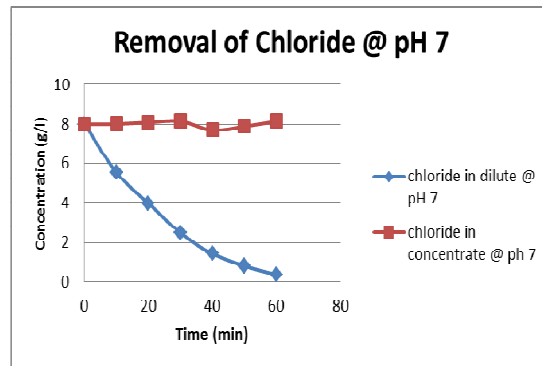


Figure 5 The fate of the chloride

The chloride was removed to 0.389 g/l from the initial concentration of 8g/l. Thus in an hour and with the neutral pH 95 % of the chloride was removed. Being a monovalent the chloride is removed easily [5].

3.2.2 Fate of Boron

The concentration of boron was 8 mg/l as per the analysis results of the backwater in the summer analysis. The synthetic solution was made using boric acid and sodium chloride. The diluate chamber and the concentrate chamber were filled with 8 g/l of chloride and 8 mg/l of boron. Before the analysis, the electro dialysis was flushed out with the distilled water and later as the conductivity reduced a slight saline water was used for the flushing. The experiments were done for different pH measures. The first analysis was done in a neutral pH as it was found in the site. The experiments were done and the samples were analysed in every 10 minutes to analyse the removal efficiency.

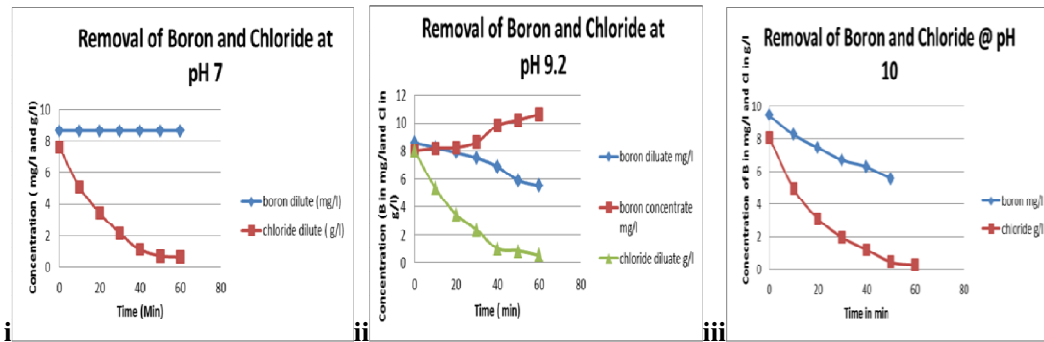


Figure 6 The fate of boron at (i) neutral pH, (ii) at pH 9.2, (iii) at pH 10

The removal efficiency of the boron at neutral pH remains 0%. Usually boron exists in the form of Boric acid in water. At pH less than 7 boron exists largely as un-dissociated boric acid $B(OH)_3$ while at pH greater than 10, $B(OH)_4$ ion will be the dominant component. Between these pH values highly water soluble polyborate ions are formed [6]. The electro dialysis being a method which removes charged ions failed to remove the boron at neutral pH. Thus it is found that the speciation and pH have a significant role on boron removal. The removal of boric acid by reverse osmosis is also limited in neutral pH. [7]

The 2nd set of analysis was done with a higher pH of 9.2 because boric acid dissociates at pH 9.2 to borate ions [6], [8]. The pH was raised to 9.2 by adding 0.1 N NaOH. Thus at pH 9.2 the boric acid dissociates to borate ion and these borate ions are transferred through the membrane. The removal efficiency found out was about 30 %. But it was not up to the Indian standards specified which 1 mg/l was (IS: 10500, 2012). The full removal of the boric acid is not achieved due to the lack of complete dissociated of boric acid to borate ions.

The pH was raised to the maximum pH of 10 that the membrane could handle as per the characteristics of the membrane. At pH 10 the boron removal rate was increased to a percentage of 41%. But still the concentration did not reach the limit. Hence the pH has to be raised again to higher levels. The increased removal rate is the higher rate of dissociation of boric acid to borate ions. According to the previous studies [6] an efficiency of 80% is expected at pH above 10.5. From the mass balance equation the ions removed from the diluate chamber is almost equivalent to mass obtained in the concentrate container. Hence boron will not cause any significant fouling problem to the membranes. The performance of chloride remains the same with a removal efficiency of 93%.

3.2.3 Fate of Sulfate

The concentration found in the backwaters was 1.5 g/l. The synthetic solution was made with sodium sulfate and sodium chloride. The experiments were done for 1 hour and the samples were taken for every 10 minutes. The experiments are done for two different pH levels. The pH was raised using 0.1 N NaOH. The sulfate SO_4^{2-} ions were removed to an efficiency of 72% and chloride to an efficiency of 95%. There was a sudden removal of chloride and as chloride was removed considerably the removal of sulfate gained a faster pace. This is due to the competition of monovalent and divalent ions [9]. Sulfate ions being a divalent ion are removed after 76% of chloride was removed. Thus sulfate needs more time to reach the IS standards. The crystal ionic radius of sulfate (0.215 nm) was more than that of chlorine (0.164 nm) hence there is a higher chance of chloride to be removed first. At a higher pH there was no significant change in the removal efficiency of the sulfate. The removal efficiency of sulfate at pH 10 was 72% which was similar to that at neutral pH. Hence there is no dependency of pH on the removal.

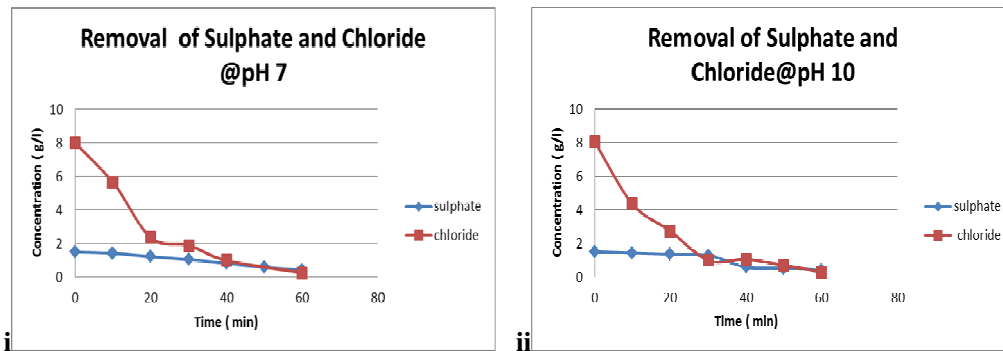


Figure 7: The fate of sulfate at (i) pH 7 and (ii) pH 10

3.2.4 Fate of Magnesium

The concentration found in the backwaters was 2.5 g/l. the synthetic solution was made with magnesium chloride. As MgCl already added chloride to the solution the amount of sodium chloride was added to compensate the remaining concentration of chloride to have a concentration of 8 g/l in total. The experiment was done for 1 hour and the analysis was done for every 10 minutes. 94% of Magnesium and 93% of chloride was removed at a pH of 7. Again Mg^{2+} being a divalent, the rate of removal of the magnesium was reduced by the interference of the monovalent. But magnesium being a cation does not show any competence with the chloride. But it should be having a competence with other monovalent anions.

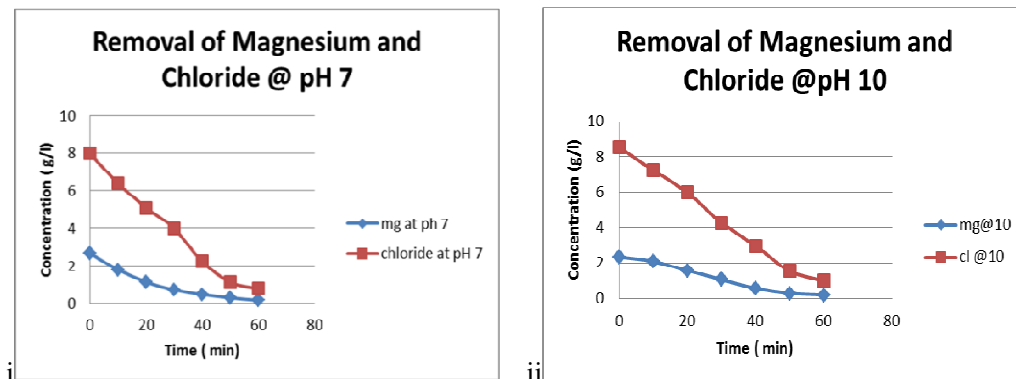


Figure 8 Fate of Magnesium at (i) neutral pH and (ii) at pH 10

3.2.5 The Fate of All the Contaminants Together.

All the three contaminants were mixed to their respective concentrations as found in the analysis and passed through the electro dialysis for a period of 1 hr. All the contaminants behaved similar to the analysis done individually. The removal rates of contaminants were, chloride 94%, boron 41%, magnesium 94%, and sulfate 65%. Only the rate of removal of sulfate was reduced. That was because on the encounter of the boron ions which again increased the competition. Magnesium being a divalent ion will have a higher rate after the removal of chloride and boron. Hence there is no significant difference in the removal when the contaminants are together.

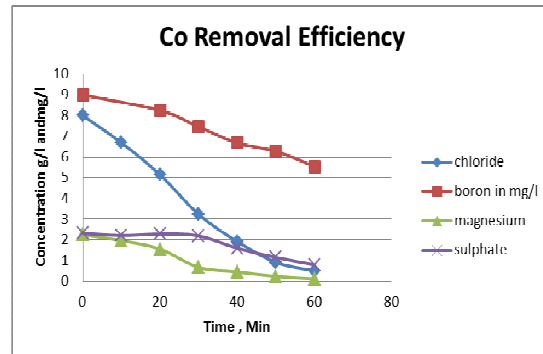


Figure 9 Fate of contaminants together at pH 10

4. Conclusions

The Boron and sulfate showed a lower reduction of 41% and 72% in an hour of desalination. The Magnesium and the chloride were removed by more than 90% in an hour. It was found that to remove boron there is a need a higher pH (greater than 10) which implies that the present membrane (AMX and CMX) used cannot be used for the efficient removal of the Boron. All other contaminants studied was not affected by the variation of pH. There were no significant difference in the removal efficiency of chloride, magnesium and boron when treated together. But the removal efficiency of the sulfate was reduced due to the presence of more anionic species.

Due to the speciation of Boron the removal is possible only at higher pH. Hence a two stage removal is necessary. But this can be advantageous as the second stage can help to remove the lower concentrations of the contaminants as their removal efficiencies are not affected by the variation of pH. As the electro dialysis works with the charge and ions the pH can be raised without the introduction of the chemicals but with the charged spacers [10]. Hence the desalination can be done without any addition of chemicals.

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