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Application of electrodialysis for recovering sodium carbonate and sodium bicarbonate from Lake Van

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ABSTRACT

Sodium salts have a crucial role, both in industrial chemical processes and in daily life. In practice, sodium carbonate and sodium bicarbonate are known as soda. Soda is an important resource; in food industry as baking soda, and in chemical industry with its whitener and anti-lime properties. Lake Van is the largest lake in Turkey. It is located in eastern region and has 6 billion ton soda reserve, which makes it the largest natural soda source in Turkey. In this study, the performance of electrodialysis (ED) for recovering the soda content in Lake Van is investigated. It is found that by applying ED on Lake Van water, the concentration of the soda can be increased from 14,000 up to 25,000 ppm, with a single unit ED in 60 min. Investigating and characterizing the ED parameters from this perspective in a deeper analysis paved the way for reducing the production time and increase in the cost efficiency of the soda industry.

Keywords: Lake Van; Soda; Electrodialysis; Sodium carbonate; Sodium bicarbonate

1. Introduction

Sodium carbonate and sodium bicarbonate (mainly known as soda) are amongst important chemicals in the human life. The areas of usage for these minerals are very wide and large, including glass (53%), chemical (24%), detergent (11%), paper (2%), textile (4%), and other (6%) industries [1]. Soda has a yearly production of almost 400 billion tons worldwide and 1 billion ton of this amount is produced in Turkey [1]. Under these circumstances, cost effectiveness and efficiency of soda derivative production become very important.

Membrane processes are occasionally used in the industrial process water treatment and desalination processes. The use of this technique varies from food production to the biotechnology as well as drinkable water production. The prevailing membrane separation processes are reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), electrodialysis (ED), and electrodeionization (EDI) [2].

Nowadays, the use of ED in desalination processes and recovery of ions from waste water and sea water is becoming ever more popular [3]. ED is an electromembrane process that uses an electric field to attract and repulse the salt components in aqueous solutions. This process can be combined with most of the current soda production methods, which rely on pretreating water with chemicals and running an evaporation/dewaterization process. More concentration in the source water would result in larger amounts of soda produced per batch. This would mean ED could become an amenable method factor in soda production if it could provide low cost and ease in application.

Last decade, Shcoeman has shown that ED has become a highly efficient and economically viable desalination method for leachate, as well as being able to produce good quality water by reducing chloride and arsenic in the process as well [4]. He estimates a 100 m^3/d batch ED plant to cost US$0.6 million, and have an operational cost of US$0.38/$m^3$ water processed. It is comprehensible that an ED-based soda production facility will even be more cost-effective considering the difference of purpose and criteria for results, as a soda production facility will process much smaller amounts of water relatively, and will not have high standards for post-processed water quality. But if so intended, there are earlier works, such as Turek study on Dual-purpose desalination-salt production ED, which even suggest such facilities to produce two valuable products [5]. His case study was on seawater in Japan, and the products were tapable water, and salt, which could to be replaced with soda in this case.

There are also promising works relating to the efficiency of the ED process, like Sadrzadeh and Mohammadi [6] evaluation study on optimum flow rates for current efficiency parameter, and Raissouni et al.'s study [7] on membrane types and specifications. Moreover, studies like Turek et al. [8] have further optimized the process by adding physical and chemical components to the ED unit.

With such improvements on ED technology and research, interest was shown in studies of potential ED applications on removal of nitrate from brackish groundwater's [9] in addition to other, more traditional desalination studies [10]. The technology is becoming so much more applicable that there are even studies on recovery of organics from aspartame effluents with ED processes [11].

Thus, the basis for potential application of ED on natural-source soda production facilities was established and further investigation on practical potential was deemed worthy.

Although ED is used for recovering various ions from various water resources, there has been scant study on recovering soda derivatives as mentioned above. In this study, the capability of ED in recovering the soda derivatives sodium carbonate and sodium bicarbonate from the water of Lake Van is investigated. The investigation is based on a single unit ED process under constant potential of 15 V for 60 min, using the laboratory type ED [12] instrument.

2. Electrodialysis

ED uses the potential difference to transfer the ions in addition to or against concentration gradient of ions through ion exchange membranes that selectively separates ions. The studies were started in late nineteenth century and commercialized in 1960s [2] is mostly used for desalination of sea water for potable water production, purification of glycerin, and handling the waste waters from various ions point of views. In ED, the electric field drives the various salt ions in the aqueous solution that the cations move towards the cathode by passing through a cation-exchange membrane and anions moving towards anode by transmitting through an anion-exchange membrane (Fig. 1).

The arrangement of the membranes in a cascade structure lets the fed solution to be separated into two different streams. The electric field and the voltage differences cause this separation with the help of the perm-selectivity of the ion-exchange membranes.

The ED process can be applied in three different operation types as *Batch*, *Continuous*, and *Feed* and *Bleed*. In batch ED, the solution is continuously recirculate through the system and the concentrated solution is passed through the system repeatedly, up to the limiting current density (LCD) and concentrations [13]. In continuous ED, feed solution passes through the ED system one time, but a cascade structure with more than one ED units may be applied in this operation mode [14]. Differing from these, in Feed and Bleed mode is operated both continuous and batch at the same time by continuously feeding and getting product while some of the product is recycled for increasing the quality [15].

3. Lake Van

Lake Van is a volcanic barrier lake located at the eastern side of Turkey, and has 3.713 km^2 area (Fig. 2). The lake itself is salty, strongly alkaline, and has high soda content. It is also the largest soda-containing lake in the world. The pH of the lake is around 9.8 and the average depth is 171 m with an average altitude of 1,646 m from sea level.

The composition of the anions and cations in waters of Lake Van are given in the Table 1 [17]. The estimated soda reserve in Lake Van is around 6 billion tons.

When the level of economic development in the regional area (Lake Van Area) is taken into consideration, any possibility for realization of this source will greatly contribute to the local and national economy.

4. Materials and methods

In this study, an experimental setup consisting of a laboratory type ED [12] unit with 10 cell pairs in the

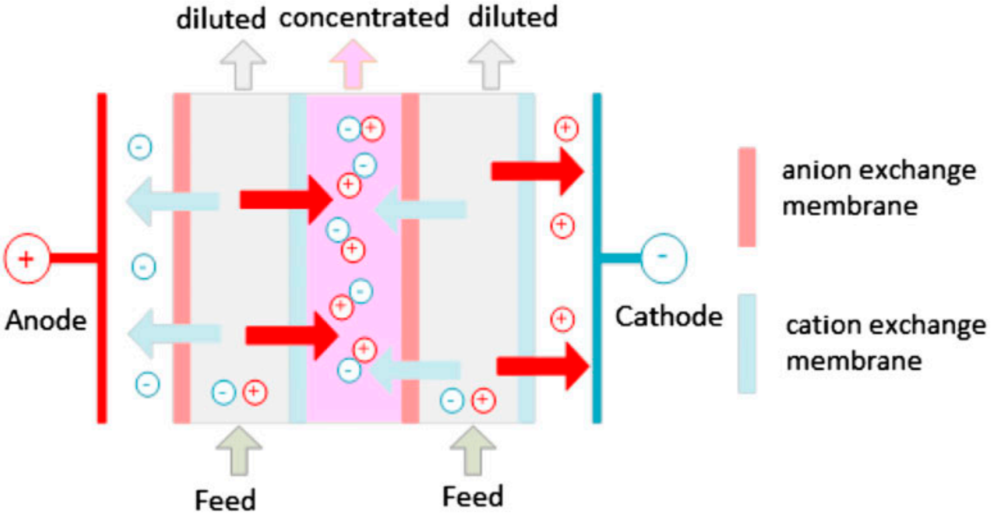

Fig. 1. ED system.

Fig. 2. Map representation of Lake Van in Turkey (Map Data: Landsat, Basarsoft, Google) [16].

system that are mounted with RALEX® ion exchange membranes (Fig. 3) are used. The concentrate and dilute are collected in separate tanks and the system repeatedly runs in batch mode operation for determined time. But it is also possible to change the membrane cell unit in a manner which enables a continuous operation on source material. The samples from Lake Van are used in the investigation after filtering in order to avoid membrane blockage. The composition of the introduced solution (lake water) is same as given in the Table 1 in laboratory conditions of 25˚C and 1 atm.

The conductivities, temperatures, and pH values are measured online using a computer connected to ThermoLab conductivity and pH meters during the experiments. The concentration of the ions in the solution is calculated using a calibration curve between the conductivity and concentration. These data are gathered by using an ion chromatograph and the remaining concentrations for the ED operation is calculated depending on this.

In the early stage of the experiment, the potential at LCD value is determined experimentally for sake of efficient operation and cost reduction [18]. In order to achieve this, a polarization curve is drawn for this system. Two regions of this relation are linearly correlated and the intersection point of them is marked as LCD.

Table 1
The compositions of the anions and cations in Lake Van (Adapted from [17])

T (℃)	5.06	Na (ppm)	8,031.04	Br (ppm)	14.52	^{72}Ge (ppb)	0.987
pH	9.52	K (ppm)	384.30	F (ppm)	3.19	^{55}Mn	1.198
ECA (μS/cm)	18,313.0	Ca (ppm)	655.38	Li (ppm)	0.95	^{56}Fe	82.980
EC25 (μS/cm)	29,579.0	HCO$_3$ (ppm)	919.60	NH$_4$ (ppm)	0.00	^{9}Be	0.000
TDS (g/L)	19.220	CO$_3$ (ppm)	3,859.31	NO$_2$ (ppm)	0.00	^{27}Al	66.210
Sal	18.03	Cl (ppm)	6,993.74	NO$_3$ (ppm)	9.78	^{47}Ti	31.340
DO (%)	54.9	Mg (ppm)	502.50	PO$_4$ (ppm)	0.00	^{51}V	51.990
DO (g/L)	6.14	SO$_4$ (ppm)	2,065.75	^{66}Zn (ppb)	0.000	^{52}Cr	142.400
^{75}As (ppb)	290.7	^{95}Mo (ppb)	18.26	^{137}Ba (ppb)	5.874	^{165}Ho	0.044
^{82}Se (ppb)	121.2	^{101}Ru (ppb)	0.02	^{141}Pr (ppb)	0.003	^{166}Er	0.080
^{85}Rp (ppb)	218.1	^{105}Pd (ppb)	1.62	^{146}Nd (ppb)	0.05	^{169}Tm	0.027
^{88}Sr (ppb)	19.0	^{107}Ag (ppb)	0.37	^{153}Eu (ppb)	0.009	^{172}Yb	0.035
^{89}Y (ppb)	0.349	^{133}Cs (ppb)	1.94	^{157}Gd (ppb)	0.031	^{175}Lu	0.018
^{90}Zr (ppb)	95.82	^{115}In (ppb)	0.018	^{159}Tb (ppb)	0.005	^{178}Hf	0.396
^{93}Nb (ppb)	0.571	^{121}Sb (ppb)	0.92	^{163}Dy (ppb)	0.033	^{69}Ga	0.405
^{181}Ta (ppb)	1.757	^{182}W (ppb)	184.00	^{185}Re (ppb)	0.019		
^{59}Co (ppb)	0.195	^{60}Ni (ppb)	0.00	^{65}Cu (ppb)	21.980		

Fig. 3. Laboratory type ED system setup.

The experimental study has been carried out in constant voltage batch mode for unlimited time that system is left to reach limits. This value is fixed at 60 min for this ED operation since it seems that this value is enough after preliminary investigation. The flow rate of the treated water sample is 50 L/h (Table 2).

In these conditions the ED operation is maintained and conductivities, pH, and temperatures of dilute and concentrate are recorded in order to investigate the ion concentration in the solutions during the ED process.

Finally, the specific power consumption (SPC) is calculated by integrating the current vs time relation with operating potential in order to find the total power consumed in the ED process in given time per unit volume of solution.

5. Results and discussion

In order to determine the working potential, LCD has been determined by applying various constant potential to ED system and the current values are measured. The potential at LCD can be seen from Fig. 4 that 20 V is the intersection point of the trend lines of two sections. Thus, 15 V is taken as operation

Table 2
The operating limits of the laboratory ED unit [2]

Parameter	Value
Effective area of ED module (cm^2)	1,344
Effective area of one membrane (cm^2)	64
Number of membrane pairs in ED module	10
Spacer thickness (mm)	0.8
Electrodes (anode, cathode) (pc/Ti+Pt)	2
Operating voltage (V/Membrane pair)	1–1.2
Maximum voltage (V)	24
Maximum current (A)	2
Operating flow rate (L/h)	45–65
Operating temperature (℃)	20–30

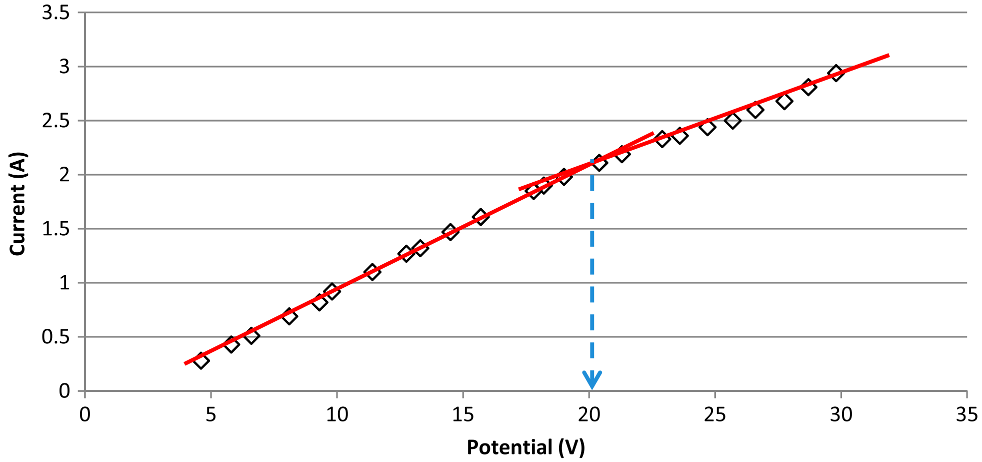

Fig. 4. Polarization curve and determination of the LCD.

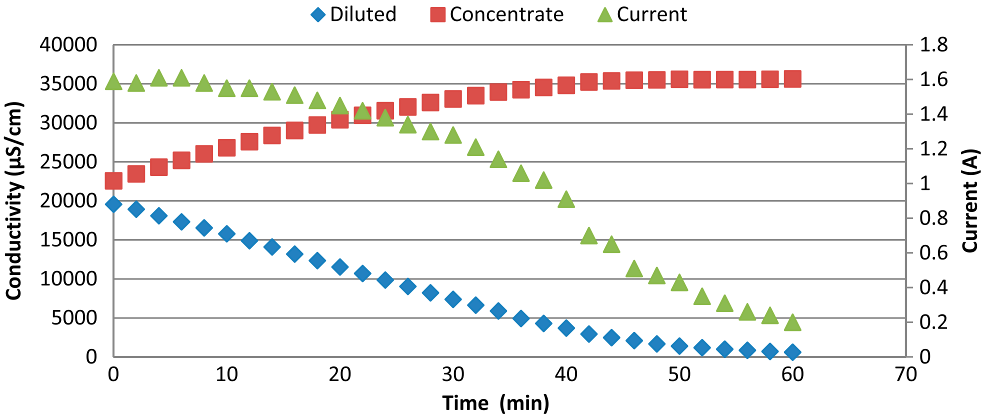

Fig. 5. Conductivity and current variation by time.

potential for remaining calculations as 75% of the LCD.

As the streams taken into account for a precise investigation ion chromatography is needed, a relevant discussion can be made from the conductivity and the concentration profiles of the ions. Histories of conductivities for both diluted and concentrated streams and current are given in Fig. 5. While the conductivity of the feed solution is increased up to 35,000 µS/cm in the concentrate within batch time of 60 min, the conductivity of dilute stream dropped down to 600 µS/cm. Current values through the batch time are steadily decreasing from 1.6 to 0.2 A since the ohmic resistance increases as the diluted stream becomes leaner through the ED process.

Concentration profiles with respect to the batch ED time are given in Fig. 6 for concentrate and dilute. These concentrations are related to the presence of ions Na^+, K^+, Ca^+, CO_3^{-2}, HCO_3^{-1}, and Cl^{-1}. The tendency of the concentration is similar to the conductivity values and it is seen that the concentration of the concentrate reached up to 24,000 ppm. It can be concluded from Fig. 6 that after 45 min, the concentrate and dilute reached to the limit. Only small portion of the ions are left to transfer. This situation can also be seen from the current values also, as after 45 min, the current values dropped lower than 0.5 A and converged to final value. This leads us to conclude that the experiment time is sufficient for the operation.

The pH level in the concentrate in the sample solutions during the ED process is stabilized in the value of 9.6, whereas, the dilute pH value dropped up to 9.1 from 9.8 as it is seen in Fig. 7.

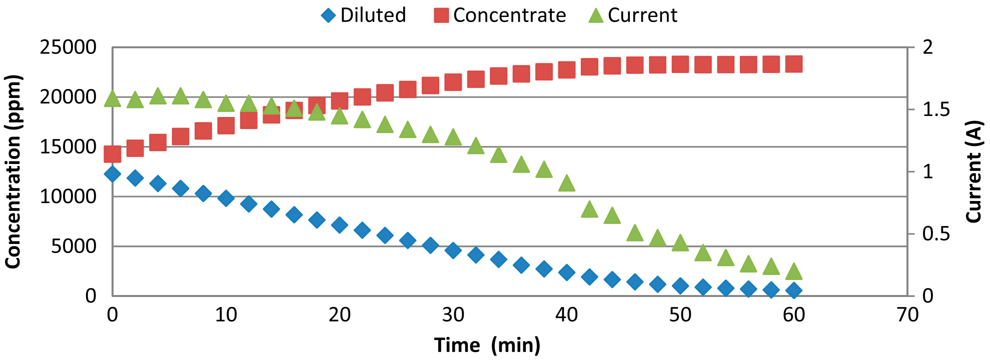

Fig. 6. Concentration and current variation by time.

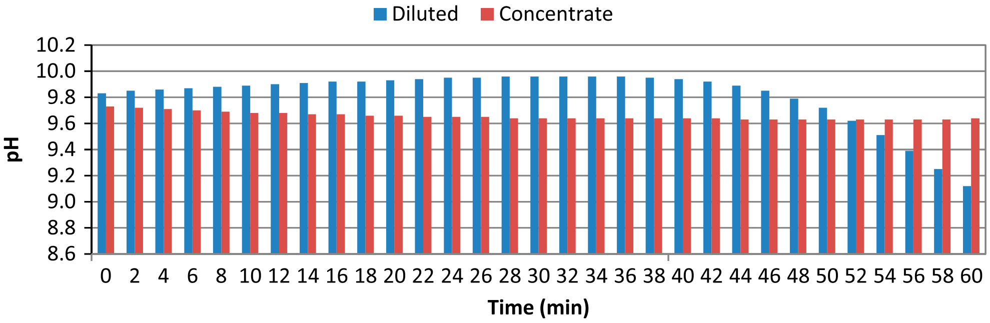

Fig. 7. pH variation by time.

The recovery of the ions in the feed is reached up to 95.41% by this single stage constant potential ED system. That shows us the capability of the application of ED process for recovering the ions in Lake Van.

The SPC for this ED operation is calculated according to the Eq. (1) [19] and found as 0.539 kWh/L of fed solution that correspond to 48.5 US$/t. The membrane cost is around 50 US$/t for this operation when optimum current density is applied as discussed by Strathmann in details [20]. As a result, total cost for production is going to be around 100 US$/t, and this value is much lower than the current price state of the sodium carbonate and sodium bicarbonate which is around 300 US$/t [21] in the market.

$$\mathrm{SPC} = \frac{E\int_0^t I dt}{V_o} \tag{1}$$

6. Conclusion

This study aimed to show that the soda potential in Lake Van can be turned into account by using ED process. With the results, it is seen that the potential of the ED for this operation is considerably high. The ED system increased the concentration of the soda content to 1.75 times the fed concentration; this increment is expected and also can be increased further by a proper optimization study.

It can be said that the soda recovery from Lake Van by using ED process in an earlier stage than the evaporation—the product of ED process will be proposed as the brine feed to the evaporative soda production—the cost and time of the production will be considerably decreased. The total ED system will cost about 100 US$/t for preparing concentrated brine and this will decrease the soda derivatives price dependently. Total capacity of the production will also be doubled since the crystallized concentration of soda components will increase [22].

The results showed that the soda concentration in the brine is increased up to 25,000 ppm with 15 V in 60 min. Further studies will be conducted for optimizing the ED system. This optimization must cover maximizing the concentration increment in the brine while keeping the working SPC minimum as possible by taking the parameters of voltage, time, and operation principle as variables. Also the efficiency of the cascade system should be investigated.

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