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RESEARCH ARTICLE

Boron rejection from aqueous solution and wastewater by direct contact membrane distillation

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ABSTRACT

Boron is widely used in various areas of modern technology. Due to the environmental problems arising during the production and use, the studies on the removal and recovery of boron from wastewater have been increased recently. Membrane distillation (MD) system is smaller in size with respect to other common distillation systems and needs lower operating temperatures. In addition, the equipment costs are reduced and the safety of the process increases since it operates at lower pressures. Moreover, the membrane distillation process can remove pollutants from water without using chemicals. In this study, boron rejection from aqueous solutions and wastewater was investigated by using direct contact membrane distillation (DCMD) system where both surfaces of a porous hydrophobic membrane were in contact with liquid streams. The effects of various parameters (pH, feed concentration, feed temperature, etc.) on boron rejection were investigated and the highest boron rejection was found to be 50 % when pH=10 at 50 °C and with feeding by a pump of 54 rpm. According to the test results of wastewater from Kırka Borax treatment plants, the mean distillate fluxes were found as 13, 16 and 14 L m^{-2} h^{-1} at the feed temperatures of 30, 40 and 50 °C, respectively. The boron removal percentages were found to be 47, 64 and 48 % at 30, 40 and 50 °C, respectively. It was observed in the XRD spectra that the crystals in wastewater mainly consist of $Na_2B(OH)_4Cl$ and $Mg_2B_2O_5$ structures.

Keywords: Boron, membrane distillation, recovery, rejection, wastewater

1. INTRODUCTION

Various environmental problems arise during the production of boron minerals, compounds and derivatives and as a result of the use of boron in many industrial areas. Although a boron product can replace another boron product in some cases, there is not another substitute that can provide the same quality and affordability as boron compounds. As the use of boron compounds becomes widespread, it also brings environmental problems. In the Water Pollution Control Regulation in Turkey, the boron level limitation is 0.3-1 mg L^{-1} for the water that can be used as irrigation water while the boron level limit in drinking water is given as 0.5 mg L^{-1}. The limit value for boron is given as 500 mg L^{-1} in discharge standards of mining industry wastewater [1].

Boron is normally present as boric acid and borax ions in water. Boric acid is a very weak monobasic acid with a special structure. It does not give protons in aqueous solution but it receives electrons and holds OH- ions (Eq. 1).

$$B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+ \qquad K=5.8*10^{-10} \qquad (1)$$

During the formation of boric acid, the B^{3+} cations draw oxygen and as a result of this attraction the O-H bonds are broken and BO_3^{3-} anions are formed. The radius of the B^{3+} cation is very small (0.23 A°) and therefore it is not found free in nature. The compounds of boron with oxygen are abundant due to the great attraction to oxygen. Boron formation varies depending on the pH of the water. $B(OH)_3$ is dominant in acidic waters (pH <6) [2]. Tetra-penta-hexa and other polyborates are found in natural and alkaline waters. The dissolution of alkali metallic borates is

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faster in the solutions with medium pH values in comparison with other solutions and the dissolution rate of borates generally increases as temperature increases. Boric acid dissolves more quickly in hot water with respect to cold water.

Eti Mining Operations General Directorate Kırka Boron Plant has 930.000 tons year^{-1} production capacity. The products produced in this establishment are tincal, boraxpentahydrate, anhydrous borax and calcined tinkal. In this plant, the water used in the first washing of the boron mineral taken from the quarries and the waters coming from the other processes are sent to the settling pools and kept in these pools. There are 7 settling pools. The waste ponds cover much more area than the plants. There are a drainage channel surrounding the plant and a secondary water collection pond connected to it so that the ponds do not overflow and damage the agricultural lands due to rainfall. The collected water is delivered to the waste ponds by a pump. A total of approximately 400,000 tons year^{-1} of waste is generated in the Eti Maden Kırka Boron Plants. These wastes cause environmental problems and they also have some content of boron minerals of high strategic importance.

The direct contact membrane distillation (DCMD) method for boron removal from water and wastewater is a relatively new technology that is an alternative to conventional separation methods. In DCMD, evaporation occurs at the feed-membrane interface and condensation occurs at the distillate-membrane interface. The hot feed solution and the cold distillate solution are in direct contact with the surfaces of the membrane in the feed and distillate regions, respectively. The steam formed on the feed side is carried from the membrane to the distillate side due to the pressure difference. The feed does not enter into the membrane due to the hydrophobic characteristic of the membrane. Only the gas phase formations can enter into the membrane pores. The DCMD is the most commonly used membrane distillation (MD) configuration because it is suitable for laboratory trials. The main disadvantage of this method is that the heat loss by conduction is high. In the DCMD method, the temperature of the feed solution is below the boiling point. The feed and distillate pressures are close to atmospheric pressure. For all membrane distillation types, the distillate flux is calculated by measuring the condensed flow collected on the distillate side of the membrane. DCMD is suitable for water applications in which the feed solution contains non-volatile components such as salts, colloids, proteins, etc.. This method is also used in some applications such as desalination, reuse of water, food processing and pharmaceuticals [3-5].

The advantages of membrane distillation separation over other conventional separation methods are as follows:

1) It requires lower operating temperatures (feed: 30-80 °C, distillate: 15-30 °C) and lower steam pressures with respect to the other distillation processes.

2) Lower operating pressures are used with respect to the pressure-driven membrane processes such as reverse osmosis. This is because high pressure is needed to overcome the osmotic pressure for concentrated solutions in reverse osmosis. Furthermore, a more efficient treatment for high concentration solutions or wastewater can be achieved with DCMD.

3) 100% (theoretical) retention of non-volatile solutes can be achieved.

4) It consumes less energy compared to the multi-stage vacuum evaporation method.

5) There is reduced chemical interaction between the membrane and the process solution [3].

There are many studies in the literature that remove boron from low concentration wastewater, groundwater or aqueous solutions (Table 1).

Table 1. Literature studies using the membrane distillation method

Membran Type	Flux	Results	Reference
PTFE	40 kg m^{-2} s^{-1}	DCMD; 2 M NaCl feed, T_b=55 °C Ts=15 °C salt removal (>99.8%)	[6]
PP	650 L m^{-2} d^{-1}	DCMD; tap water, feed ve distillate T_b=353 ve T_s=293 K, removal >75%	[7]
SMM(PS)M1	2.45.10^{-6} m s^{-1}	DCMD; T_b=50 °C, T_s=40 °C, feed solution is 0.5 M NaCl, salt removal: 99.9 %	[8]
PVDF	10.5 kg m^{-2} s^{-1}	DCMD; feed: hot boric acid solution, T_b=50 °C T_s=40 °C boron removal (>99.8%)	[9]
PVDF	7.5 kg m^{-2} s^{-1}	DCMD; feed: super saline solution T_b=59 °C, T_s=20 °C	[10]
PVDF	20 kg m^{-2} s^{-1}	DCMD; feed: 4.5 M NaCl T_b=60 °C T_s=20 °C	[11]
PP	16 L m^{-2} h^{-1}	DCMD; feed: boron mine wastewater T_b=40 °C T_s=20 °C, boron removal (%64)	This work

In this study, the effectiveness of the DCMD method on the removal of boron from the high concentration wastewater of the factory extracting boron mine was investigated. In this study, the efficiency of boron uptake from aqueous solution and actual wastewater using direct contact membrane distillation method was investigated under various conditions. In the experiments carried out for this purpose, the concentrated feed solution taken from the waste water of the Kırka Borax Plant was crystallized and the obtained solid products were characterized.

2. MATERIALS AND METHOD

After the membrane distillation system was installed, the membrane (polypropylene, MD020TP 2N, Microdyn-Nadir Gmbh, Germany, containing 40 capillary tubes with a pore diameter of 0.2 μm) was activated before proceeding to preliminary trials. The activation involves washing for 1 hour with distilled water followed by washing with 50% by volume isopropanol aqueous solution for 1 hour.

First, pure water passes through the activated membrane to obtain a regular flux. The flow rates were adjusted using a peristaltic pump. The rpm value of the pump is called flow rate in this study. The feed and distillate currents were passed through the membrane module according to the countercurrent principle. The effects of the initial pH, feed temperature, feed boron concentration and feed flow rate on performance were investigated while the distillate temperature was kept constant at 20 °C. Furthermore, at the end of each experiment, a cleaning process was applied to prevent the contamination of the membrane. Pure water, 1% by mass NaOH aqueous solution, and 1% by mass $C_6H_8O_7$ aqueous solution were passed through the membrane consequently in the cleaning process. Each step was performed at 30 °C for 30 minutes. The experimental setup is shown in Fig 1.

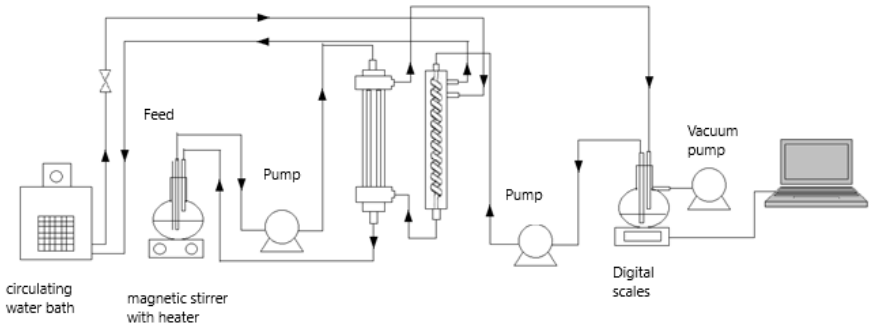

Fig 1. Schematic representation of the experimental system

The distillate stream was continuously weighed on the precision balance and the obtained value was transferred to the computer every 30 seconds. The flux and percentage of the boron retention were calculated from Equations 1 and 2 given below.

$$\text{Flux(J)}=\Delta W(kg)/[A(m^2)*\Delta t*(h)] \quad (1)$$

$$\text{Boron retention \%} = [(C_f-C_d)/C_f]*100 \quad (2)$$

Here, ΔW is the amount of distillate measured at certain time intervals, A is the membrane surface area (0.0889 m^2), Δt is the time at which the amount of distillate is recorded, C_f is the boron concentration in the feed and C_d is the distillate boron concentration.

3. RESULTS & DISCUSSION

3.1. Effect of initial pH

In the experiments performed for examining the effect of initial pH on boron retention, the solution with a boron concentration of 100 mg L^{-1} was adjusted to different initial pH values (2, 4, 6, 8, 10 and 12) and passed through the membrane. The pH values of boron solutions were adjusted using NaOH and HCl solutions at different concentrations and measured with a pH meter. The feed temperature was 50 °C, the flow rate was 54 rpm, the distillate temperature was 20 °C and the flow rate was 24 rpm. The collected distillate was automatically weighed on a precision scale and the results were transferred to the computer over a period of time. The fluxes were determined. The membrane was cleaned at the end of each experiment. As can be seen in Fig. 2 and Fig. 3, the distillate flux changed between 6 and 9 L m^{-2} h^{-1} between the pH values of 2 and 12. The boron retention reached 25% at low pH and 50% at high pH.

3.2. Effect of feed temperature

In the experiments carried out for examining the effect of feed temperature on boron retention, the solution at a boron concentration of 100 mg L^{-1} was adjusted to different temperatures (30, 40, 50 and 60 °C) and passed through the membrane. The feeding pH was kept constant at 10, the flow rate was 54 rpm, distillate temperature was 20 °C and flow rate was 24 rpm. The collected distillate was automatically weighed on a precision scale and the results were transferred to the computer over a period of time. The fluxes were calculated. At the end of each experiment, the membrane was cleaned. Fig 4 shows the variation of the distillate flux with feed temperature. The highest distillate flux (7.5 L m^{-2} h^{-1}) and boron uptake (50% uptake) were obtained at 50 °C.

3.3. Effect of feed concentration

In the experiments for examining the effect of feed concentration on boron uptake, the solution was passed through the membrane at different concentrations (50, 100, 250, 500, 750 and 1000 mg L^{-1}). The feeding pH was 10, temperature was 50 °C, flow rate was 54 rpm, distillate temperature was 20 °C and flow rate was 24 rpm. The collected distillate was automatically weighed on a precision scale and the results were transferred to the computer over a period of time. The fluxes were calculated. The membrane was cleaned at the end of each experiment. Fig. 5 shows the variation of the distillate flux with

feed concentration. The fluxes ranged between 5 and 7 L m^{-2} h^{-1} while the highest boron uptake was found to be 52% at a concentration of 100 mg L^{-1}.

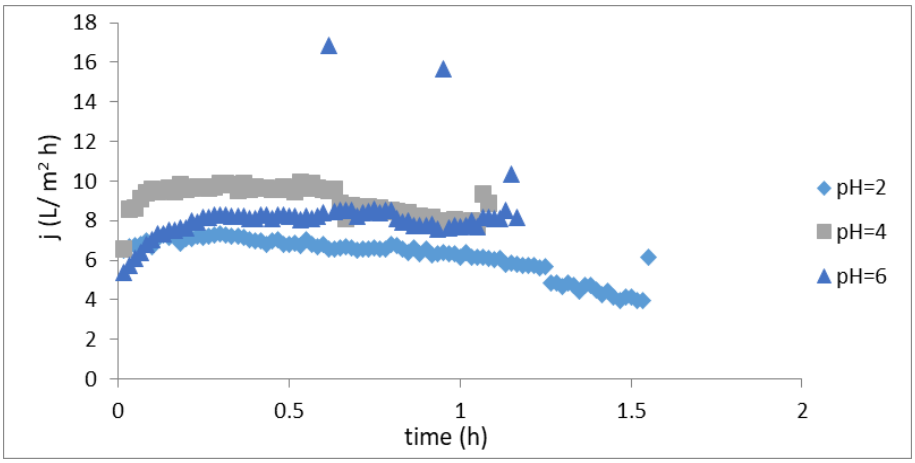

Fig 2. Variation of distillate flux with feed pH

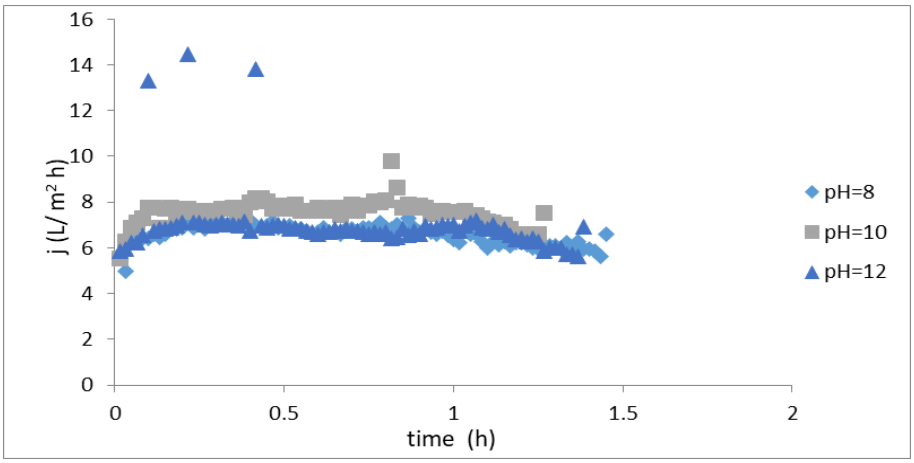

Fig 3. Variation of distillate flux with feed pH

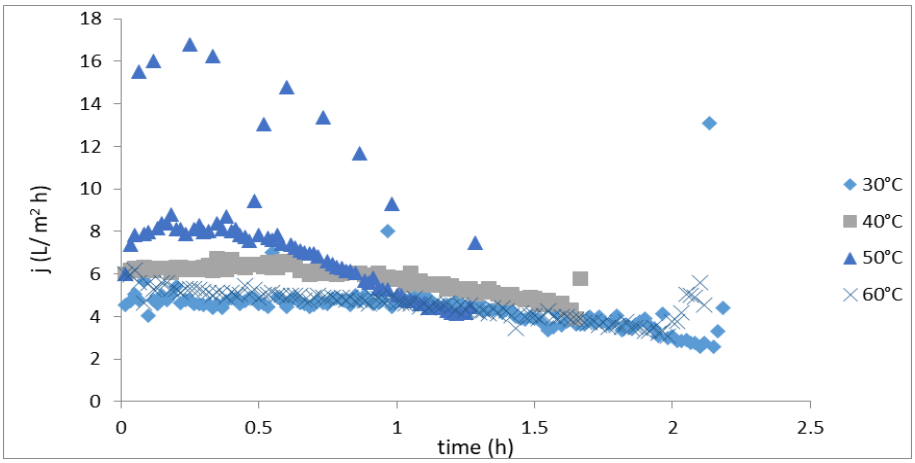

Fig 4. Variation of distillate flux with feed temperature

3.4. Effect of feed flow rate

In the experiments carried out to investigate the effect of feed flow rate on boron retention, a 100 mg L^{-1} solution was passed through the membrane at different flow rates (54, 75 and 90 rpm). The feeding pH was 10, distillate temperature was 20 °C and flow rate was 24 rpm. The collected distillate was automatically weighed on a precision scale and the results were transferred to the computer over a period of time. The fluxes were calculated. The membrane was cleaned at the end of each experiment. Fig 6 shows the variation of the distillate flux with feed flow rate. The fluxes ranged between 7 and 9 L m^{-2} h^{-1} while the highest boron retention was 50% at 54 rpm.

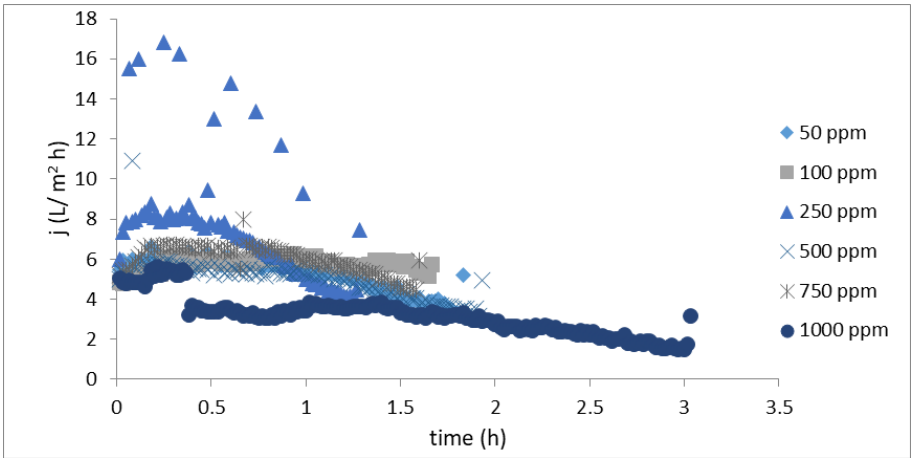

Fig 5. Variation of distillate flux with feed concentration

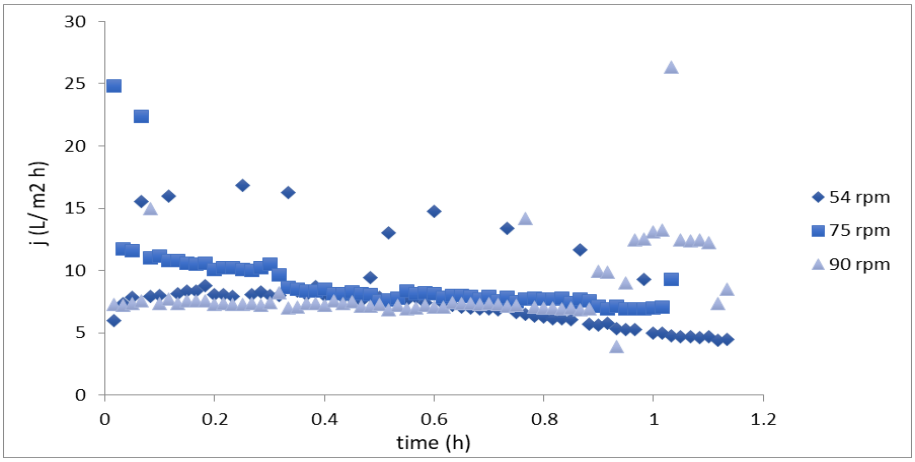

Fig 6. Variation of distillate flux with feed flow rate

3.5. Wastewater experiments

Boron is one of the most used elements in the world due to its superior properties. It is especially important to develop boron removal and recovery techniques from wastewater. The boron contained in the concentrate stream can be recovered as boron crystals by crystallization or evaporation methods. Boron crystals recovered from wastewater can be used in the nuclear field, defense industry, jet and rocket fuel, soap, detergent, solder, photography, textile dyes, glass fiber and paper industry. In this study, boron recovery studies were carried out by removing the water in the concentrated feed stream by evaporation and obtaining boron crystals. First, the wastewater from Eti Kırka Boron Plant was analyzed and the results are given in Table 2. The very high boron concentration of Eti Kırka Boron Plant wastewater is not suitable for the membrane system. A pretreatment was carried out in order to deliver the wastewater sample containing a high amount of boron to the membrane system. Precipitation experiments were carried out using calcium hydroxide. In experimental studies, 500 mL of raw wastewater was taken into beakers. Different amounts of calcium hydroxide (10 and 25g) were added to these samples and mixed for different times (2 and 4 hours) and at different temperatures (80 and 90°C) at 250 rpm and then left to settle. After the precipitation, the samples were filtered and the boron analysis of the clear part was made. Boron removal increased to 85.7% in 90 °C and 2 hours mixing time. The boron concentration in the waste water sample taken from Kırka boron plant was reduced from 3800 ppm to 500 ppm by pre-precipitation using $Ca(OH)_2$. After that, DCMD experiments were started. The feed system (wastewater) flow rate was 54 rpm and distillate flow rate was 24 rpm. The wastewater was heated to 30, 40 and 50 °C to observe the changes in the distillate flux (Fig 7). According to Fig 7, the average distillate fluxes for 30, 40 and 50 °C feed temperatures were found to be 13, 16 and 14 L m^{-2} h^{-1}, respectively. With increasing temperatures, the boron removal percentages are 47%, 64% and 48%, respectively. At the end of the experiment, the XRD and SEM analyzes of the obtained crystals were performed (Fig 8-13). The SEM analyzes of the contaminated membranes (Fig 14) were also performed.

Table 2. Characterization of wastewater

pH=9.79	
Analysis Type	**Amount**
Boron analysis (mg L^{-1})	3800
Sulphate analysis (mg L^{-1})	900
Suspended solid (mg L^{-1})	243
COD (mg L^{-1})	600

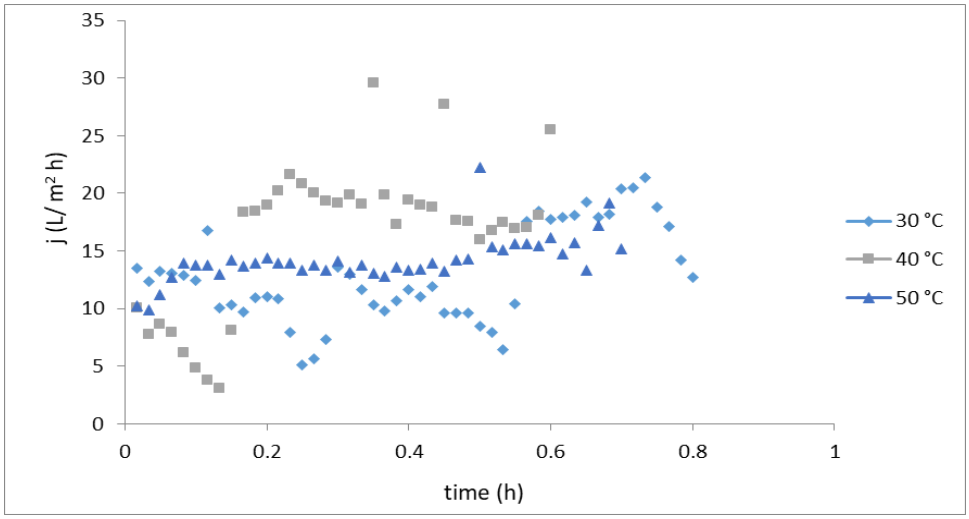

Fig 7. Variation of distillate flux versus time for wastewater

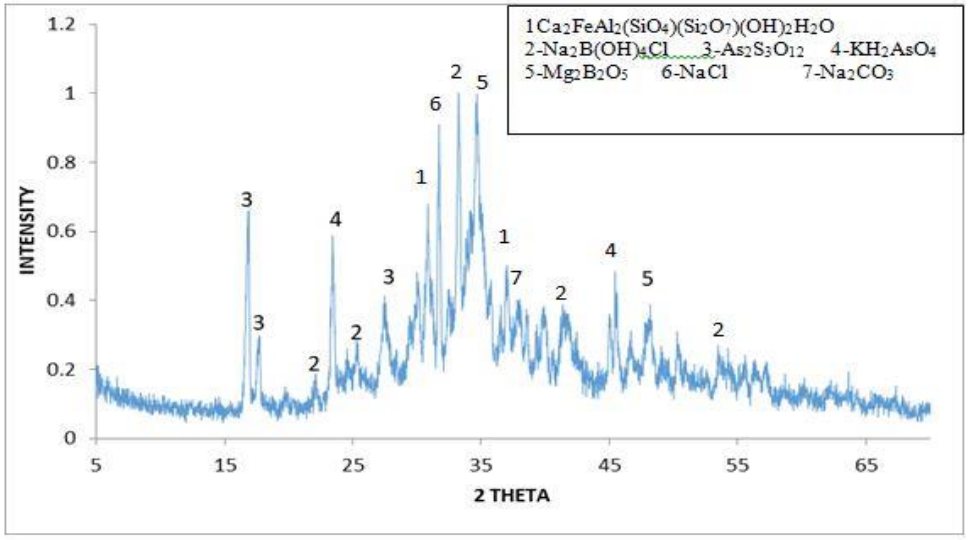

Fig 8. XRD of the crystals obtained from wastewater at 30 °C

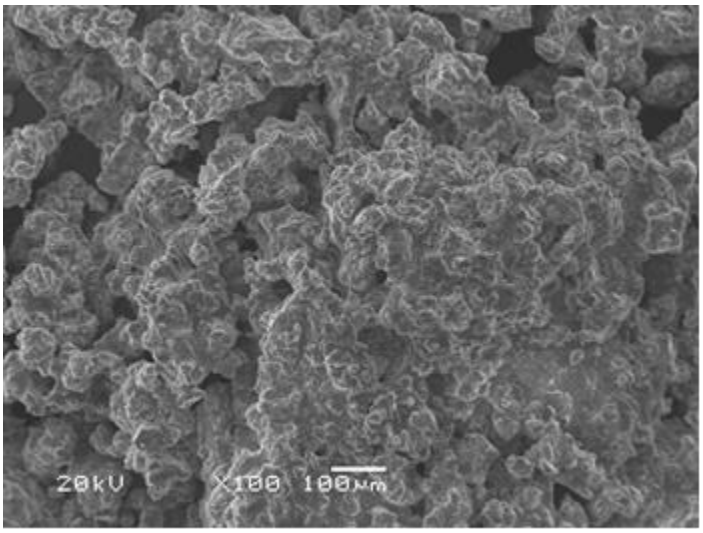

Fig 9. SEM image of the crystals obtained from wastewater at 30 °C

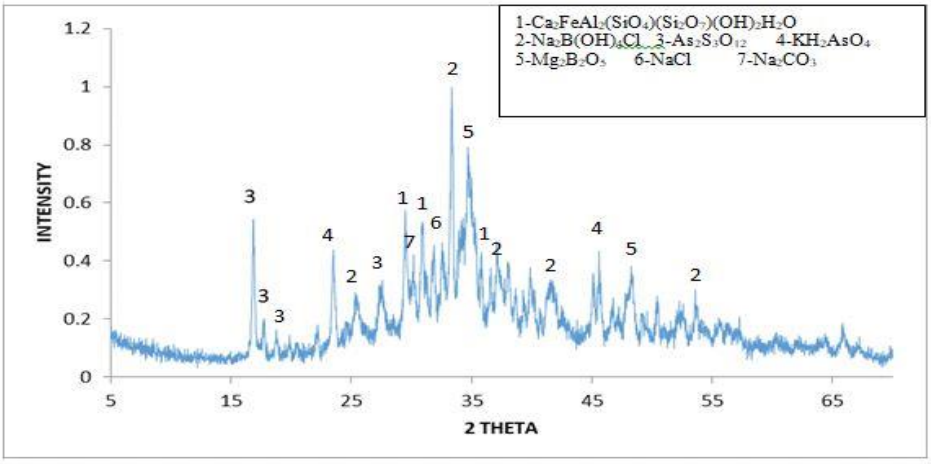

Fig 10. XRD of the crystals obtained from wastewater at 40 °C

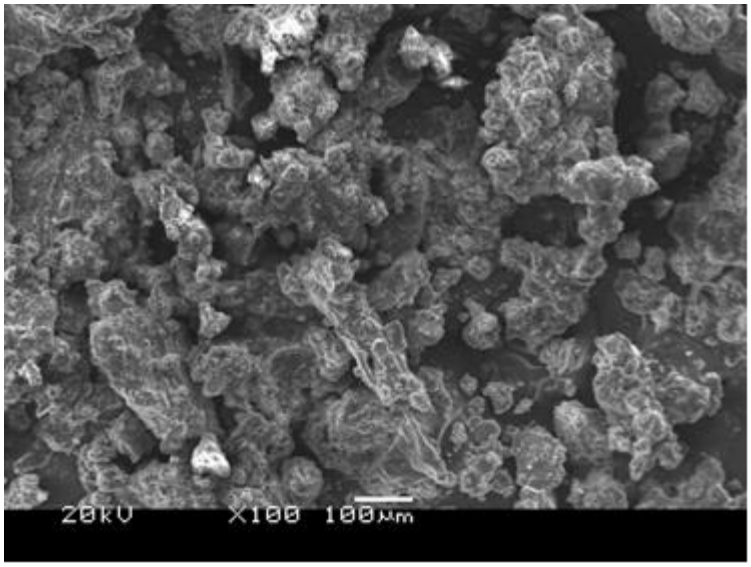

Fig 11. SEM image of the crystals obtained from wastewater at 40 °C

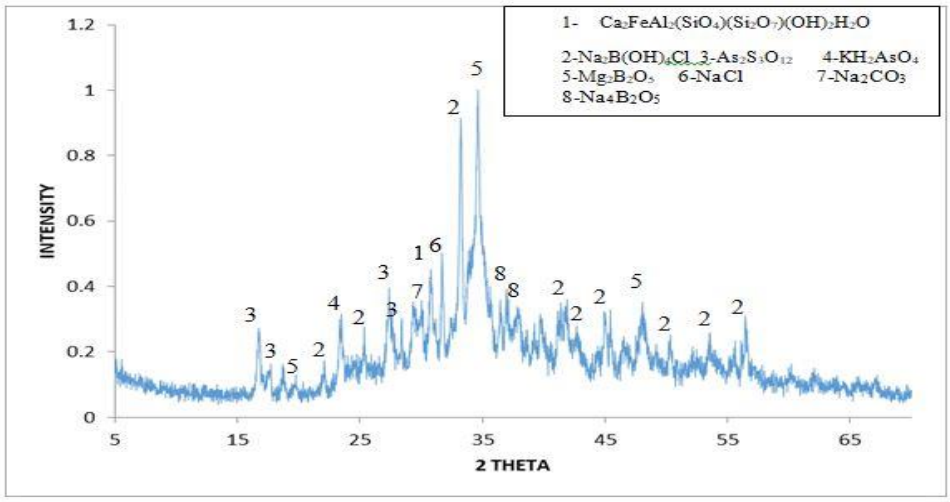

Fig 12. XRD of the crystals obtained from wastewater at 50 °C

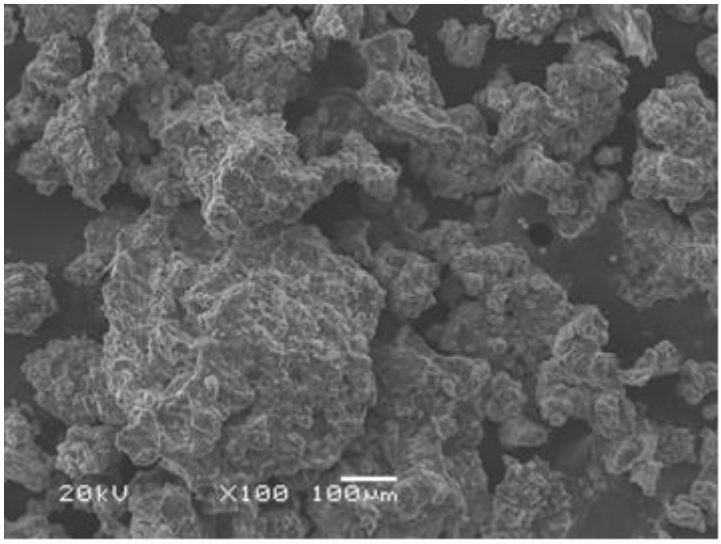

Fig 13. SEM image of the crystals obtained from wastewater at 50 °C

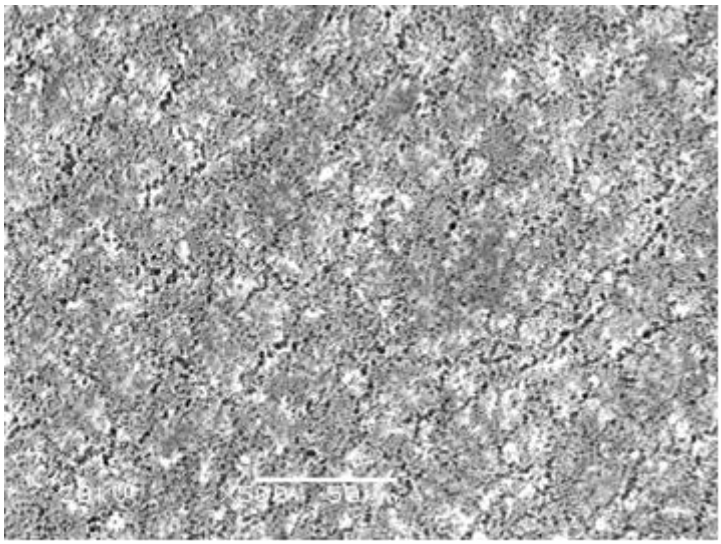

Fig 14. SEM image of the used membrane at the end of the MD experiments using wastewater

4. CONCLUSIONS

Boron is present as boric acid in water below pH=9. In waters above pH=9, borate anions are in the form of $B(OH)_4^-$. The hydrated larger diameter borates at higher pH values are better retained by the membrane in comparison with boric acid at lower pH's. The highest boron removal was found to be 50% at pH=10.

The highest distillate flux (7.5 L m^{-2} h^{-1}) and boron removal (50% removal) were obtained at 50 °C. Usually, there is a linear relationship between the temperature difference of the feed and the distillate and the flux. The greater the temperature difference between the two solutions which come into contact with the two separate surfaces of the membrane, the greater the difference in water vapor pressure which is the driving force for mass transfer. On the other hand, as the temperature rise increases the rate of evaporation, the formation of concentration polarization is also accelerated. Therefore, in the membrane distillation process, it is necessary to determine the optimum conditions for the temperature and flow rate of the feed solution.

The highest boron removal rate was found to be 52% at 100 mg L^{-1} concentration. Increased concentration of feed solution reduces water vapor pressure and drive power. Thus, the increase in concentration leads to a decrease in distillate flux and boron removal.

In the membrane distillation process, the distillate flux is also related to the flow rate. The shear forces at high flow rates prevent particles from accumulating on the membrane surface. Thus, fouling formation on the membrane surface is reduced. However, in the experiments where the flow rate was examined, the flow rate could not be reached to very high values according to the data obtained in the preliminary studies. The fluxes ranged between 7 and 9 L m^{-2} h^{-1} while the highest boron removal was 50% at 54 rpm. The effect of high flow rates could not be investigated due to the very rapid tearing of the hose.

The optimum pH value was found as 10 in the study. Therefore, the pH (9.8) of the wastewater of Kırka Boron Plant was not changed. For wastewater

experiments, the optimum flow rate found in the previous experiments was used. Therefore, only the temperature of the feed could be studied for wastewater. According to the test results, the average distillate fluxes for the feed temperatures of 30, 40 and 50 °C were found to be 13, 16 and 14 L m^{-2} h^{-1}, respectively. Boron removal percentages are 47, 64 and 48%, respectively, with the increasing temperatures.

The feed solution was crystallized at different temperatures. The SEM images of the obtained crystals are not very different from each other. In SEM images of crystals, amorphous layered, plate-like structures have been observed. Boron element is generally found in nature as borate salts or boric acid. Metals such as sodium, calcium, magnesium are found in the structure of boron minerals. In XRD shots, the crystals mostly contain $Na_2B(OH)_4Cl$ and $Mg_2B_2O_5$ structures although the peak intensities are different. Due to the use of real wastewater, various organic and inorganic contaminants were found in wastewater. Therefore, different compounds other than boron were observed in XRD results.

At the end of the experiments with wastewater, crystals were deposited on the membrane according to the SEM image of the membrane used. Therefore, membrane cleaning was performed at the end of each experiment. Higher boron removal efficiency can be achieved when this method is applied to waters containing lower concentrations of boron such as geothermal waters.

Along with the capital costs (system investment, auxiliary equipment investment, installation fees, security and control system, etc.) of an MD setup, thermal (energy required for both heating the aqueous feed solution and cooling the permeable aqueous solution or condensate) and electrical (required for operating circulation pumps, vacuum pumps or compressors) energy consumption, energy cost, capacity, feed water quality, optimum flow conditions, long term MD performance, fouling and membrane life, facility life, operation and maintenance (O&M), depreciation, annual operating costs should be considered. The capital cost depends on the capacity and design of the MD system. Fig 15. shows the percentage contribution of different cost elements to capital and O&M expenses for the proposed MD plant in the base case and waste heat integration case. Thermal energy accounts for the largest share of O & M for the base case. Electricity and membrane replacement are the biggest contributors to O&M for waste heat integration situation.

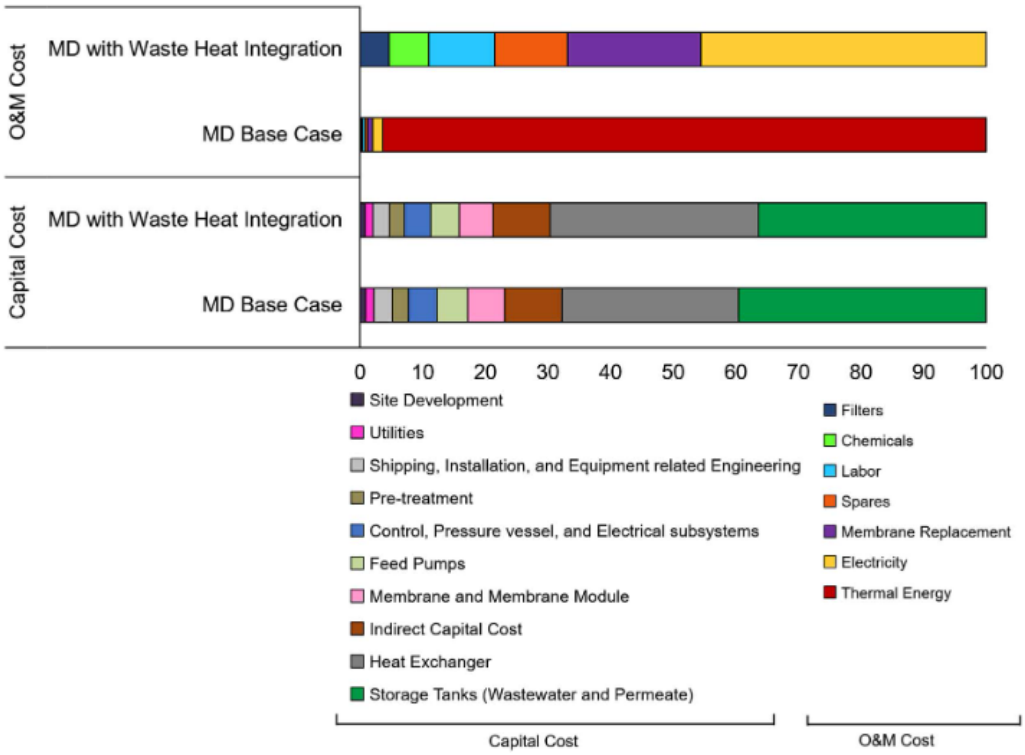

Fig 15. Fractional contribution of capital and O & M costs by various cost elements for base case and MD with waste heat integration scenarios [12]

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REFERENCES

[1]. Official Gazette, Regulation on Water Pollution Control, No 25687, 31 December 2004.

[2]. V. Kochkodan, N.B. Darwish and N. Hilal, "The chemistry of boron in water, boron separation processes," Elsevier 1st ed., pp. 35-62, 2015.

[3]. M. Khayet, T. Matsuura, "Pervaporation and vacuum membrane distillation process: modeling and experiments," *AIChE Journal*, Vol. 50(8), pp. 1697-1712, 2004.

[4]. A. Alkhudhiri, N. Darwish and N. Hilal, "Membrane distillation: A comprehensive review," *Desalination*, Vol. 287, pp. 2-18, 2012.

[5]. P. Onsekizoğlu, "Effects of osmotic distillation and membrane distillation applications on product quality in apple juice production," Doctorate Thesis, Hacettepe University, Ankara, 2010.

[6]. L. Li, Y. Guan, F. Cheng and Y. Liu, "Treatment of high salinity brines by direct contact membrane distillation: effect of membrane characteristics and salinity," *Chemosphere*, Vol. 140, pp. 143-149, 2015.

[7]. M. Gryta, "Water purification by membrane distillation process," *Separation Science and Technology*, Vol 41, pp. 1789-1798, 2006.

[8]. M. Qtaishat, M. Khayet and T. Matsuura, "Novel porous composite hydrophobic/hydrophilic polysulfone membranes for desalination by direct contact membrane distillation," *Journal of Membrane Science*, Vol. 329, pp. 1-2, 193-200, 2009.

[9]. D. Hou, J. Wang, X. Sun, Z. Luan, C. Zhao and X. Ren, "Boron removal from aqueous solution by direct contact membrane distillation," *Journal of Hazardous Materials*, Vol. 177 pp. 613-619, 2010.

[10]. R. Bouchrit, "Direct contact membrane distillation: capability to treat hyper-saline solution," *Desalination*, Vol. 376, pp. 117-129, 2015.

[11]. C. M. Tun, J. T. Fane and M.R. Sheikholeslami, "Membrane distillation crystallization of concentrated salts-flux and crystal formation," *Journal of Membrane Science*, Vol. 257, pp. 144-155, 2005.

[12]. S. Tavakkoli, O. R. Lokare, R. D. Vidic and V. Khanna, "A techno-economic assessment of membrane distillation for treatment of Marcellus shale produced water," *Desalination*, Vol. 416, pp. 24-34, 2017.