# Investigation of Treatment of Boron Industries Waste Waters by Nanofiltration

İbrahim Karakaş
Department of Chemical Engineering,
Engineering Faculty, Atatürk University,
Erzurum, Turkey

Recep Boncukçuoğlu
Department of Environmental Engineering,
Engineering Faculty, Atatürk University,
Erzurum, Turkey

M. Muhtar Kocakerim
Department of Chemical Engineering,
Engineering Faculty, Atatürk University,
Erzurum, Turkey

Alper E. Yilmaz
Department of Environmental Engineering,
Engineering Faculty, Atatürk University,
Erzurum, Turkey

**Abstract:** Turkey has the richest boron reserve in the world. Colemanite and Tincal, which are some of the ores produced in Turkey, are used in the production of Boric Acid and Sodium Perborates, respectively. As a result of this production process, the amount of solid waste and wastewater is quite high and in order for these wastes to not cause different environmental problems, they must either be disposed in some way or the boron they contain must be removed. In this study, the removal of boron from synthetic waters by nanofiltration was investigated. It was investigated operational parameters such as boron feed concentration, pH, pressure and flow rate at boron removal experiments. DMSO was used as complex agent and it was thought that DMSO forms a complex with water. Boron removal was not obtained at experiments, which was not used DMSO. The separation of the solid boron compound was studied in a wide range of conditions by nanofiltration (NF). The best result with DMSO was 290 ppm effluent boron concentration for 3000 ppm influent boron concentration with efficiency of 92%. In the final stage, cross-flow membrane filtration was used for the separation of solid-liquid. The result of this study showed that the boron recovery efficiency was as high as 95% from the wastewater.

**Keywords:** Boron, boron removal, membrane, nanofiltration, DMSO

## 1. Introduction

Boron is found in the form of borate in oceans, sedimentary rocks, coal, shale, and soils [1–3]. In natural waters, boron is normally found at concentrations lower than 1mg B/L [4], although in seawater boron concentration is around 5mg B/L [5]. Boron concentrations over 3mg/L result in an accumulation in soil and increase toxicity to aquatic life [5,6]. Among the different anthropogenic sources of boron are agricultural products (micro-fertilizers), insecticides, glass manufacturing, domestic products (soaps, detergents, laundry powders), fire retardants, anti-freeze formulations, power generation using coal and oil, insulation and textile-grade fibers, and mild antiseptics [1–4,6]. Boron is one of the most important micro-nutrients for plants, and is essential for plant growth. However, boron is beneficial to plants only in small quantities, as excessive amounts are injurious and even lethal. Irrigation with more than 1mg B/L is harmful to most plants [7]. The sensitivity of plants to boron ranges from values lower than 0.5 mg/L up to 15 mg/L.

Boron is a commonly known drinking water contaminant that affects the reproductability of living organisms [8]. Due to its interaction with the environment, the boron concentration in both, drinking water and wastewaters discarded to the environment, is strongly limited according to the WHO and European Union regulations [9,10]. The maximum boron level in drinking water was set at 0.5 mg/L and at 1 mg/L in the case of wastewaters discarded to the environment.

Of particular interest is the removal of boron by RO and NF membranes which are nowbeing used increasingly in sea/brackish water desalination and wastewater reclamation. At pH above

the pKa of boric acid (9.25 at 25 ◦C), the ionic borate species predominates and its removal by RO and NF membranes is relatively high [11,12]. However, at the pH of natural waters and wastewaters, boron occurs as boric acid and, consequently, the rejection of this uncharged species by RO and NF membranes is relatively low [13,14]. Therefore, meeting the stringent limits for boron in drinking water as set by the WHO and the EU (0.5 and 1 mg/L, respectively) is a major challenge when using RO/NF membranes with natural waters and wastewaters [15,16].

Boron rejection by RO/NF membranes can be increased significantly by adjusting the pH of the feed water to levels above the pKa of boric acid (i.e., pH> 9.25). For example, at pH 10, boron rejection was reported to increase to 99 and 93% for seawater and brackish water RO membranes, respectively, whereas at pH 11 the corresponding boron rejection values increased to 99.5 and 99%, respectively [17]. A specially designed, high boron rejection membrane was evaluated by Taniguchi et al. and was shown to reject 94–96% boron at pH 8. With this high boron rejection seawater RO membrane, a single-pass RO operation resulted in low boron concentration in the product water. Other combinations of seawater RO membranes followed by a selective ion exchange resin can achieve higher boron removal, but the cost may be prohibitive due to regeneration of the resins [18].

## 2. Experimental

All experiments were performed with pure solutions of boron in distilled water. The pH of the solutions was adjusted using either 0.1 M NaOH stock solution or 0.2 M HCl. All chemicals used were of reagent grade quality. In order to assess the influence of different solution properties on the rejection of boron, membrane separation experiments were performed in a bench scale membrane filtration module unit operated at 15-25 bar pressure at room temperature. The unit was equipped with either a NF membrane sheet made of polyether sulphone of 14 $cm^2$ net filtration area.

The solutions were recycled through the membrane from a 10 L feed reservoir and 10 ml permeate samples were collected for analysis as indicated. Solutions of 1500, 3000 and 4500 mg/l average boron concentration were used in the NF experiments. The influence of the feed pH on the complexation and further on membrane rejection was examined in a pH range of 6,5-11,0. All experiments were repeated 2–3 times. Fig. 1 presents a schematic description of the cross-flow test unit. Boron rejection was calculated from the measured total boron concentration in the permeate (Cp) and in the feed solution (Cf) according to the following equation:

$$\mathrm{Re}\ jection = 1 - \frac{C_p}{C_f}$$

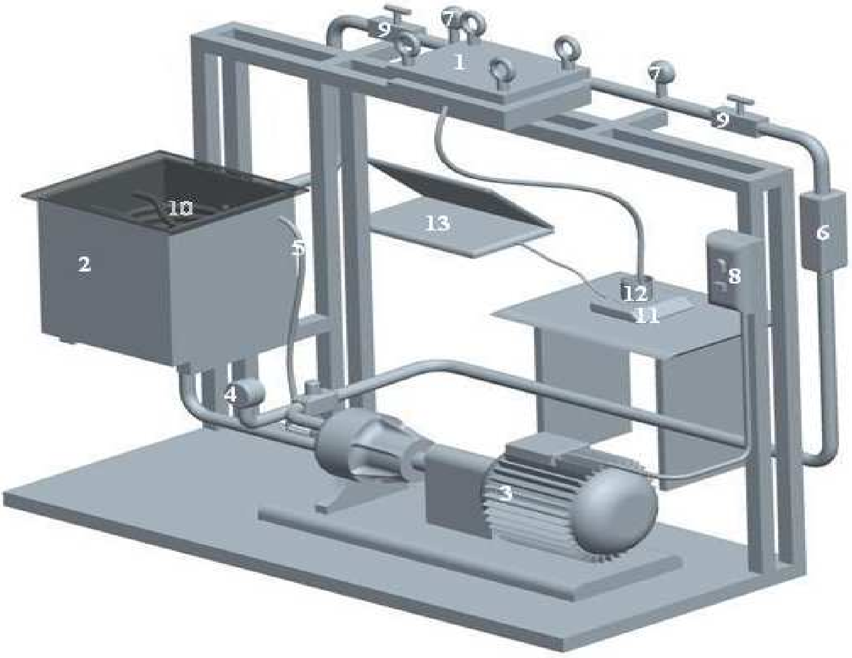

Fig. 1. Schematic description of the batch NF test unit.
1. Membrane cell, 2. Feed tank, 3. Pomp, 4. Manometer, 5. By-Pass, 6. Flowmeter, 7. Manometer, 8. Control panel, 9. Valf, 10. Changer, 11. Analytic balance, 12. Beher, 13. Computer

The parameters used experiments were shown at Table 1 and specifications of the membranes were given at Table 2.

| Parameter | Range of parameter |
|---|---|
| Pressure (atm) | 15, 20, 25 |
| Flow rate (L/dak) | 2, 4, 8 |
| Boron concentration (mg/L) | 1500, 3000, 4500 |

Table 1. Parameters used in nanofiltration experiments

| | |
|---|---|
| Material | Hydrophilic polyetersulphon |
| pH | 0-14 |
| Max. temperature | 95 °C |
| Max. operation pressure(atm) | 40 |
| MWCO (Dalton) | 1000 |

Table 2. Specifications of the membranes used in nanofiltration experiments

## 3. Results and Discussion

In this study, it was investigated to removable of boron industrial wastewater by filtration. Nanofiltration was selected as filtration process. Borax solutions with different concentration were prepared. Initial boron concentration, pH, flow rate and pressure were selected as operational parameters. Obtained experimental data shown that boron was not removed by nanofiltration process. Borate molecules size was increased with a chemical substance in order to achieve boron removal by nanofiltration. In the lied this aim, Dimethyl sulphoxide (DMSO) was added to boron solutions. These experiments were replicated.

### 3.1. The effect of DMSO amount on boron removal efficiency

To evaluate this effect, a series of experiments were performed, using solution containing boron of 4500 mg/L. The effect of DMSO amount on the boron removal was examined at 2.5, 5, 10, 20, 30, 40, 50 and 60 mL. Initial pH of 9.35, temperature 293 K, stirring time 15 min and stirring speed of 300 rpm were kept constant in the experiments. Obtained experimental results were shown graphically in Figure 2.

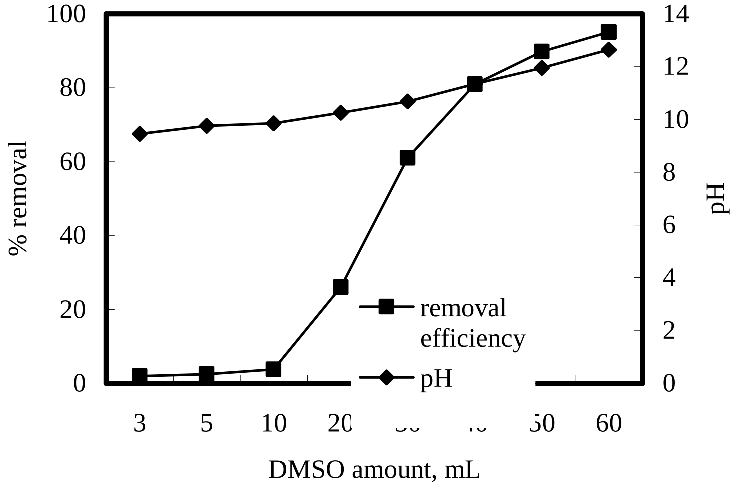

Figure 2. The effect of DMSO amount on boron removal efficiency

As seen Figure 2, boron removal increased with increasing the DMSO amount. It was thought that increasing boron removal was result from reaction between DMSO and aqueous media. Because of this reaction, a fraction of water was not used as solvent. DMSO attached to a fraction of water in solution as following reactions;

$$DMSO.2H_2O \xrightarrow{DMSO} DMSO.H_2O + H_2O \qquad (1)$$

$$DMSO.H_2O \xrightarrow{DMSO} DMSO.HOH.DMSO \qquad (2)$$

DMSO has a characteristic of compose of hydrogen band. When DMSO was added to aqueous media, it composed doughty hydrogen band. In this situation, water as used solvent decreased and borax precipitated.

### 3.2. The effect of boron concentration on boron removal efficiency

The effect of initial boron concentration on the boron removal was examined with solutions including boron of 500, 1500, 3000, 4500 and 7500 mg/L. DMSO amount of 30 mL, optimum pH of 9.35, solution temperature 293 K, stirring time 15 min and stirring speed of 300 rpm were kept constant in the experiments. The results obtained were shown graphically in Figure 3.

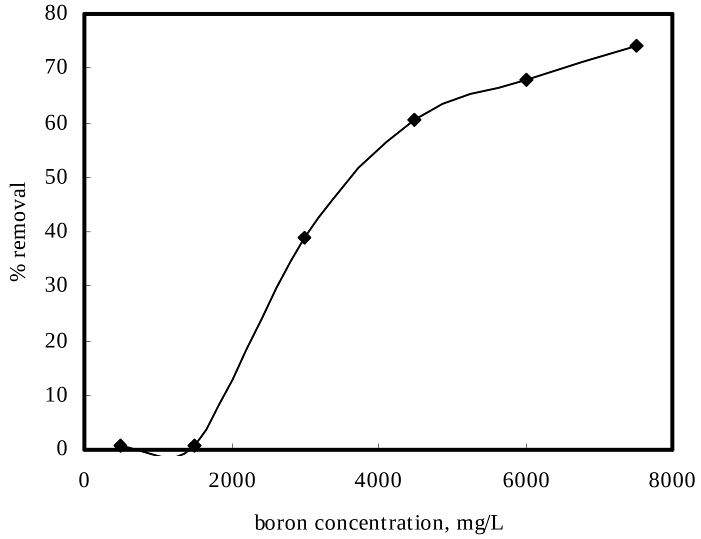

Figure 3. The effect of boron concentration on boron removal efficiency

As seen Figure 3, increasing boron concentration increased boron removal efficiency. The reason of increasing boron removal efficiency was added to constant DMSO amount to solutions. Therefore, constant DMSO amount was decreased the same amount of water as used solvent. The solutions with high initial boron concentration were reached to saturation values.

### 3.3 Nanofiltration experiments

In this section of the study, nanofiltration was investigated for removal of crystals obtained from reactions between boron and DMSO. Parameters at Table 1 were used in these experiments. The capable of filtration of solutions with boron and DMSO was investigated wit cross flow membrane filtration. The results obtained experiments shown that boron removal efficiency was highest at 15 atm pressure and 4 L/min flow rate. The results obtained from experiments investigating the effect of pressure and flow rate on boron removal were demonstrated in Figure 4 and Figure 5, respectively.

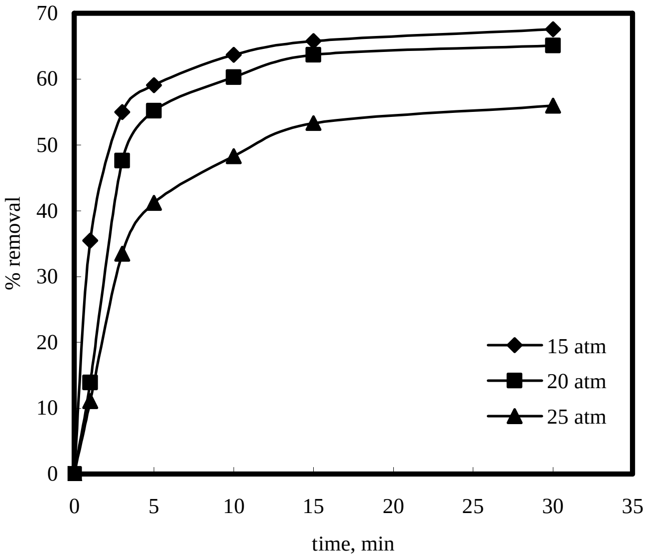

Figure 4. The effect of pressure change on boron removal (4500 mg/L boron concentration, 4 L/dak flow rate)

The results obtained from experiment with different initial boron concentration and constant DMSO amount were demonstrated graphically in Figure 6. 15 atm pressure and 4 L/min flow rate were kept constant in the experiments.

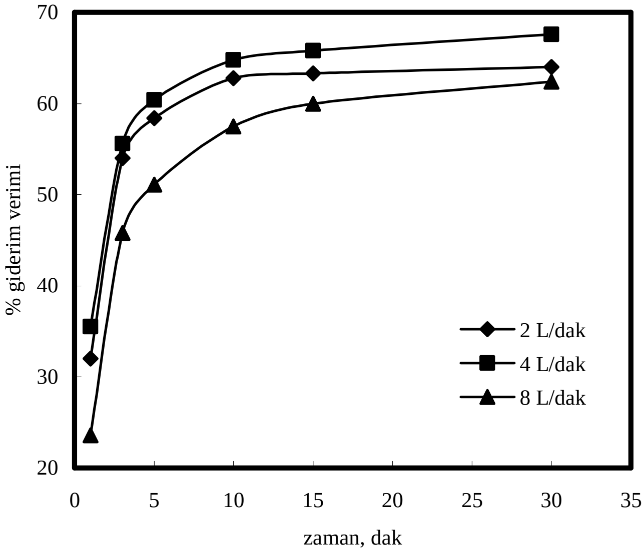

Figure 5. The effect of flow rate on boron removal (4500 mg/L boron concentration, 15 atm pressure)

As seen Figure 6, increasing initial boron concentration increased boron removal efficiency. Increasing boron concentration came near to saturation concentration of borate in solution. Therefore, increasing boron concentration increased removal efficiency with the assistance of constant DMSO amount.

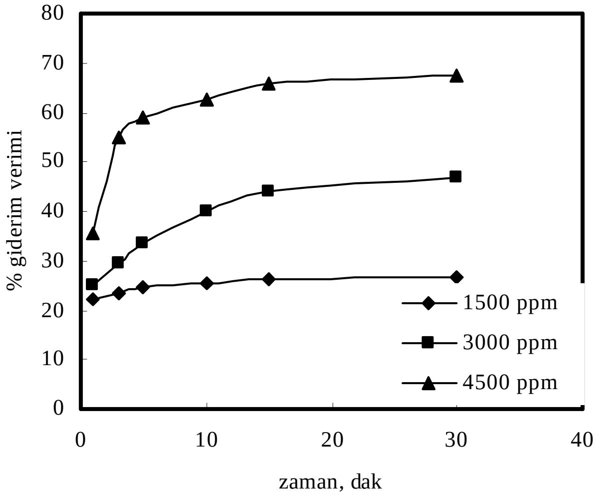

Figure 6. The effect of initial boron concentration on boron removal efficiency by nanofiltration

## References

[1] Y. Magara, A. Tabata, M. Kohki, M. Kawasaki, M. Hirose, (1998) Development of boron reduction system for sea water desalination, Desalination 118 25–33.

[2] S. Sahin, (2002) A mathematical relationship for the explanation of ion exchange for boron adsorption, Desalination 143 35–43.

[3] C. Yazbeck, W. Kloppmann, R. Cottier, J. Sahuquillo, G. Debotte, G. Huel, (2005) Health impact evaluation of boron in drinking water: a geographical risk assessment in northern France, Environ. Geochem. Health 27 419–427.

[4] D.L. Harp, (1997) Modifications to the azomethine-H method for determining boron in water, Anal. Chim. Acta 346 373–379.

[5] A.R. Dincer, (2004) Use of activated sludge in biological treatment of boron containing wastewater by fed-batch operation, Process Biochem. 39 723–730.

[6] A.E. Yilmaz, R. Boncukcuoglu, M.M. Kocakerim, B. Keskinler, (2005) The investigation of parameters affecting boron removal by electrocoagulationmethod, J. Hazard. Mater. 125 160–165.

[7] L. Melnyk, V. Goncharuk, I. Butnyk, E. Tsapiuk, (2005) Boron removal fromnatural and wastewaters using combined sorption/membrane process, Desalination 185 147–157.

[8] R.E Linder, (1990), Effects of acute exposure to boric acid on the male reproductive system of the rat. J. Toxicol. Environ. Health, 31 133–146.

[9] WHO, Guidelines for drinking water quality, 3rd ed., vol. 2, WHO, Geneva, 1998.

[10] A.J. Wyness, R.H. Parkman and C. Neal, (2003) A summary of boron surface water quality data throughout the European Union. Sci. Total Environ., 314–316 255–269.

[11] A. Sagiv, R. Semiat, (2004) Analysis of parameters affecting boron permeation through reverse osmosis membranes, J. Membr. Sci. 243 79–87.

[12] M. Taniguchi, M. Kurihara, S. Kimura, (2001) Boron reduction performance of reverse osmosis seawater desalination process, J. Membr. Sci. 183 259–267.

[13] D. Prats, M.F. Chillon-Arias, M. Rodriguez-Pastor, (2000) Analysis of the influence of pH and pressure on the elimination of boron in reverse osmosis, Desalination 128 269–273.

[14] J. Redondo, M. Busch, J.-P. De Witte, (2003) Boron removal from seawater using FILMTEC high rejection SWRO membranes, Desalination 156 229–238.

[15] Council of European Communities, Directive 98/83. (1998)On the quality of water intended for human consumption. EC Official J., L330–L341.

[16] WHO. Guidelines for drinking-water quality, first addendum to third edition, vol. 1, 2006 Recommendations, 3rd ed., WHO,

[17] C. Fritzmann, J. Lowenberg, T. Wintgens, T. Melin, (2007) State-of-the-art of reverse osmosis desalination, Desalination 216 1–76.

[18] M. Taniguchi, Y. Fusaoka, T. Nishikawa, M. Kurihara, (2004) Boron removal in RO seawater desalination, Desalination 167 419–426.