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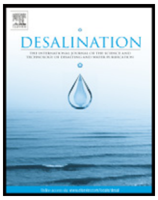

Electrodialytic separation of boric and hydrochloric acids

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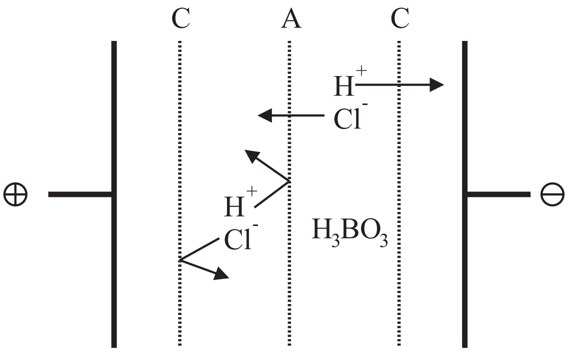
HIGHLIGHTS

- Acidic lyes from the boron sorbents regeneration were subjected to electrodialysis.
- Boric acid can be separated from hydrochloric acid by electrodialysis.
- Boric acid transport is mainly due to diffusion.
- ACM membrane showed better H_3BO_3:HCl separation than AMX membrane.

GRAPHICAL ABSTRACT



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ABSTRACT

Regeneration of boron-selective sorbents produces the acidic effluents of high boron content. Electrodialysis was proposed as a method for hydrochloric acid regeneration from the effluents composed of 0.1 kmol/m^3 hydrochloric acid and boric acid concentration ranging from 0.1 to 2.5 kg B/m^3. Boric acid mass transfer across anion-exchange membranes was investigated using a bench-scale electrodialyzer of an effective membrane area of 16 cm^2. An extended Nernst–Planck model was used for transport parameters estimation. Comparison of Neosepta AMX and ACM membranes showed that boric acid transport across the latter is much slower, allowing more effective separation of hydrochloric and boric acids. The boric acid transport in the investigated case is mainly due to diffusion of boric acid across the membrane.

1. Introduction

Boron is an essential micro-nutrient; however, at high concentrations it becomes toxic to living organisms. In humans and animals, long-term consumption of boron by food or water can cause failure of cardiovascular, nervous, alimentary, and reproductive systems [1]. Boron also increases the risk of pathological births. Boron content in many waters is higher than the permissible level in drinking water or wastewater according to the local regulations (in European countries it is usually 1 mg B/L) or the 2.4 mg B/L level recommended by WHO [2]. In the case of Poland, leachate from Tarnowskie Góry landfill contains 80 mg B/L [3], while geothermal water from Western Carpathia region was reported to have up to 97 mg B/L [4]. Boron levels in the Mediterranean region ground waters have up to 8 mg B/L [5]. Boron can be removed from aqueous solutions using selective sorbents, mainly containing N-methyl-D-glucamine as a functional group [6–10]. Boric acid reacts with the vicinal hydroxyl groups, while the protonated amine groups stabilize the resulting negatively charged esters. The sorbent regeneration is performed by first flushing the column with acid (hydrochloric or sulfuric), to desorb the boric acid, and then with sodium hydroxide, to recreate the sorbent functional groups [11]. The first step of the regeneration procedure produces acidic effluents of high boron content, which should be regenerated in order to decrease

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Table 1
Composition of consecutive effluent fractions from boron-desorption [9].

Fraction	Volume [m^3]	Boron content [kg B/m^3]	HCl content [kg/m^3]
1	1.538	2.333	17.57
2	1.455	1.845	30.34
3	3.034	0.163	1.05

Table 2
Experimental conditions for AMX and ACM membranes.

Experiment	i [A/m^2]		$C^0_{B,d}$ [kg B/m^3]	V [m^3 · 10^3]	t [s]
	AMX	ACM			
9C(2)	164	170	1.3	1.0	1800
7C(1)	164	170	2.5	1.0	1800
4 V	320	331	2.5	1.8	900
8C(1)	164	170	0.1	1.0	1800
1 V	8.48	8.50	0.1	0.1	3600
2 V	320	331	0.1	1.8	900
3 V	8.48	8.50	2.5	0.1	3600
6C(1)	8.48	8.50	1.3	0.1	3600
5C(1)	320	331	1.3	1.8	900

their negative environmental impact. Electrodialysis can be applied for this purpose.

Electrodialytic treatment of boric acid solutions of low pH has been widely studied. In the acidic environment, the boric acid remains undissociated and does not migrate in the electric field, which causes the boron removal to be relatively small. For instance, Kabay et al. [12] reported up to 20% boron removal at pH 8.5–9.0 and boron content of 25–100 mg B/L. Melnik et al. [13] reported the current efficiency of boric acid transport to be at most 1.2% during seawater electrodialysis. Low boron removal means the ionized species can be selectively removed from the boric acid solutions [14,15]. Melnyk et al. have studied the separation of boric acid from hydrochloric and sulfuric acids [16]. They proposed a post-utilization lye regeneration process involving electrodialysis and reverse osmosis [11], with the recovery of calcium borate. In the earlier papers, the concept of post-regeneration lyes utilization has been proposed [9,17]. Table 1 presents the composition of consecutive effluent fractions collected after boron desorption. In the proposed concept, fraction no. 1 is treated by electrodialysis. The acidic concentrate, having low boron content, is reused for the sorbent column regeneration. The diluate is further treated by adsorption/co-precipitation. Fraction no. 2, with higher HCl content, but lower boron content, could be directly used for boron desorption. Fraction no. 3 is recycled to the sorbent column feed.

Another possibility for post-regeneration lye utilization is the production of solid boric acid. In the earlier research, a concept of integrated ED–RO system has been proposed [18]. The first step of the process is the electrodialysis of the boric acid and salts solution at pH < 4.0. The desalinated boric acid solution is then alkalized and fed to a two-stage RO unit, which produces the boron-free permeate and retentate used in boric acid crystallization. Post-regeneration lyes could be used as an alternative boron source.

In order to properly design the electrodialysis unit for the abovementioned purposes, it is necessary to select the most suitable membrane and know the mass transfer parameters. The mass transfer across ion-exchange membrane can be described using an extended Nernst–Planck model [15,19]:

$$J_i = -D_{i,m}\left(\nabla\overline{C}_i + \frac{z\overline{C}_i F}{RT}\nabla\phi\right) + \overline{C}_i\sum\alpha_j\nu_j \qquad (1)$$

The equation combines diffusive transport caused by the concentration gradient, $\nabla\overline{C}_i$, across the membrane, electromigration caused by the electric potential gradient, $\nabla\varphi$, and convective transport caused by the interactions between *i*-th species and other species passing through the membrane, represented by their volumetric flux v_j. Eq. (1) is widely applied for the modeling of electrodialytic desalination, including boric acid transport [14,20]. In the previous paper [15], the diffusion coefficients of boric acid in the membrane were found to be $(320 \pm 40) \cdot 10^{-13}$ m^2/s, $(980 \pm 120) \cdot 10^{-13}$ m^2/s, $(235 \pm 30) \cdot 10^{-13}$ m^2/s, and $(139 \pm 12) \cdot 10^{-13}$ m^2/s, for AMX, PC-SA, AM(H) and AMV membranes, respectively. Those parameters were estimated based on the experiments performed on salt solutions of pH higher than acidic effluents from boron desorption and having much lower boron content range (0.005–0.1 mol/m^3) than in the case of post-regeneration lyes.

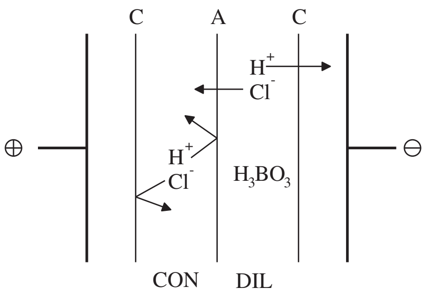

Fig. 1. Scheme of the membrane stack, C — cation-exchange membrane, A — anion-exchange membrane, CON — concentrate, DIL — diluate.

In the case of hydrochloric acid and sulfuric acid concentrations by electrodialysis, proton leakage across anion-exchange membranes is one of the main factors limiting the current efficiency, as the proton mobility in the membrane is abnormally high [21,22]. Low proton leakage membranes have been developed to assess this problem and thus from the point of view of acid concentration, the application of low proton leakage membranes may be beneficial; however, it is unclear how this type of membrane would influence the boron flux.

2. Experimental

A series of batch experiments was performed in a plate-and-frame electrodialyzer of 16 cm^2 effective membrane area. The intermembrane distance was 1 cm; the concentrate and diluate compartments had a cuboid shape of 1 × 4 × 4 cm. The membrane stack consisted of two Neosepta CMX cation-exchange membranes and one anion exchange membrane, either standard membrane Neosepta AMX or low proton leakage membrane Neosepta ACM. The AMX membrane was chosen to be a reference point for a low proton leakage ACM membrane, to assure identical conditions when comparing these two membranes. The stack scheme is presented in Fig. 1. It was previously found out that the boron flux across cation-exchange membrane is much lower than across the anion-exchange membrane [15], so it was neglected in the calculations. The solution of boric acid and 0.1 M hydrochloric acid

Table 3
Measured boron content in the concentrate compartment, LOD — limit of detection.

Experiment	Concentrate boron content [kg/m^3 · 10^4]			
	Initial		Final	
	AMX	ACM	AMX	ACM
9C(2)	2.29	2.11	10.5	3.50
7C(1)	4.53	1.61	20.6	6.79
4 V	2.58	0.635	9.26	2.52
8C(1)	0.266	<LOD	5.16	0.411
1 V	1.61	1.35	10.7	1.48
2 V	0.260	<LOD	0.550	<LOD
3 V	22.3	20.0	255	113
6C(1)	11.6	12.6	131	37.2
5C(1)	2.19	0.689	5.27	1.36