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The concept for an ED–RO integrated system for boron removal with simultaneous boron recovery in the form of boric acid

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HIGHLIGHTS

- The concept for boron removal in an integrated ED–RO system is proposed.
- Boron containing water is first desalinated by ED at low pHs, then concentrated by RO.
- RO concentration is conducted at high pHs and in the presence of D-mannitol.
- Boric acid is crystallized from the RO concentrate and alcohol is recycled for ED desalination.

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ABSTRACT

The concept of an integrated membrane system for boron removal, concentration and boric acid recovery was presented. In this system boron and polyol (e.g. D-mannitol) containing water is first desalinated by electrodialysis (ED) and then, after alkalization, concentrated by reverse osmosis (RO) in a two-stage system. The 1st RO stage permeate contains less than 1 mg/L of boron and can be then discarded to the environment or used as feed for the ED concentrate compartment. In the 2nd RO stage boron rich alkaline solution is concentrated to a retentate boron content of 10.8 g/L or more. The alkaline retentate is neutralized with a strong mineral acid and then solid boric acid crystallizes. After separation of the solid, the supernatant solution (not only saturated with boric acid but also containing alcohol and salts) is recycled back to the ED desalination step. The above concept was discussed based on the results of the design of an exemplary system in which a wastewater of 75 mg/L of boron and TDS of 1.8 g/L is treated.

1. Introduction

Boron and its compounds need to be removed from waters with high boron concentration. The necessity for boron removal and the methods applied have been thoroughly discussed in recent review papers [1–4]. It was demonstrated that in some cases boron concentration has to be reduced to at least below the value of 2.4 mg/L, which is the guideline limit for drinking water proposed by the World Health Organization (WHO). Among the suggested methods for boron removal are reverse osmosis (RO) based methods for water purification. These methods, however, face a serious limitation in boron rejection resulting from aqueous chemistry of boron containing species [1–4]. In the majority of boron containing waters, B element exists in the form of boric acid. In this form, it permeates through most of the RO membranes with ease and its rejection is strongly limited. Boric acid is a weak acid (pK_a of around 9.2) that ionizes to a significant extent only at a pH higher than 9. Upon ionization of H_3BO_3 there are mono-, tri- and tetraborates produced. These borates are rejected by RO membranes more effectively than boric acid as summarized in [1–4]. Effective boron removal from waters with high boron content, however, requires RO operation at a high pH (most likely 10 or even more) at which a serious risk of membrane scaling with insoluble carbonates, hydroxides or their mixed salts occurs. To overcome the need for high pH operation, a method of binding borate with 1,2 diol containing polyhydroxyl alcohols was proposed [5]. Mono- and dichelate complexes produced by that process are schematically presented in Fig. 1. These complexes are much more stable than monoborate, therefore they are produced even at lower feedwater pHs. These are also rejected more effectively than boric acid and monoborate, not only by RO but also by nanofiltration membranes as shown in [5–8]. These findings should have allowed for a significant reduction in feedwater pHs required to maintain sufficiently high boron rejection. It should be possible to effectively remove boron at pHs much lower than 10. This is, however, possible only at a low feedwater boron content and limited permeate recovery, due to an increase in retentate boric acid content during the process. Boric acid was shown to be the specie that determines boron transport even at pHs up to 10 [8]. To further reduce this content, an RO operation with retentate pH close to or in excess of 10 should be considered. Under those conditions, boric acid should be converted into monoborate and mono- and dichelate complexes more

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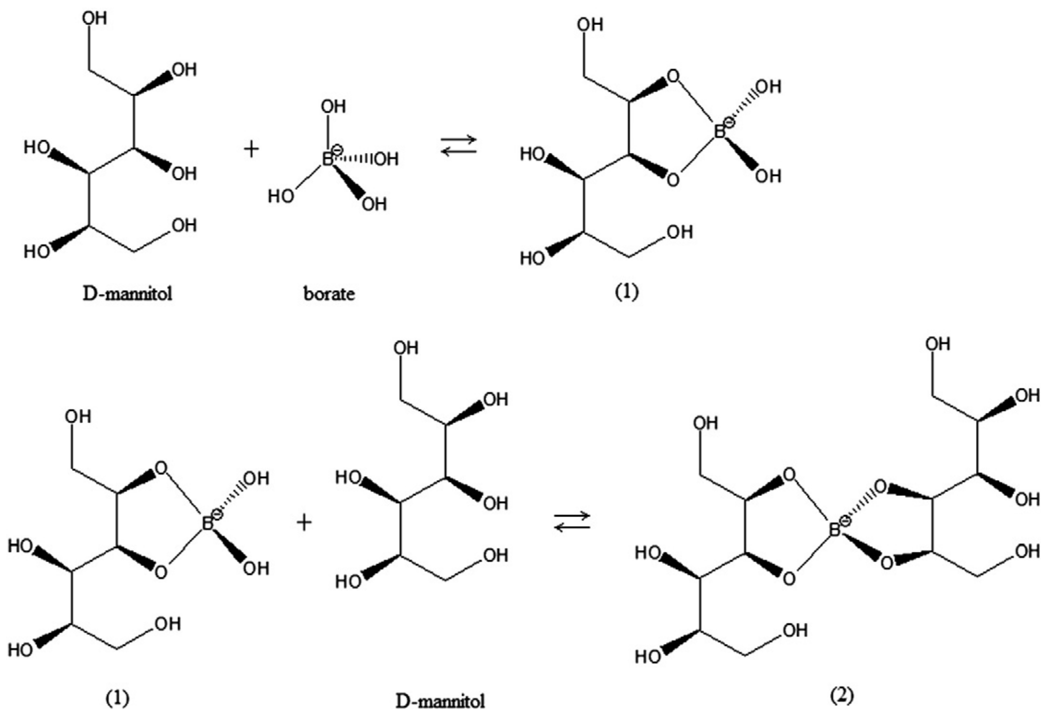

Fig. 1. Scheme of the reaction between monoborate and D-mannitol. Structures (1) and (2) represent monochelate and dichelate complexes respectively.

effectively than at lower pHs due to the equilibrium nature of the reactions in Fig. 1.

The possibility of boron removal at high permeate recovery (up to 80%) when in mixtures with polyols at pHs of 10 or higher was proven in [6]. Such high pHs, however, still implies some risk of membrane scaling with polyvalent cation (most importantly magnesium and calcium) hydroxides or carbonates. These metal cations need to be removed prior to high pH operation. As shown previously in [9–13] ionic salts can be removed from boric acid by means of electrodialysis (ED) when at low pHs. At pHs less than 4, neutral molecules such as boric acid or D-mannitol retain in ED diluate while ionic salts are removed. The alcohol–boron complex formation phenomenon also had very little effect on boron transport across ion-exchange membranes at low pHs. Therefore, the authors concluded that it should be possible to desalinate boron–alcohol–ionic salt mixtures by ED and then concentrate them using RO membranes under alkaline retentate. The latter process should result in a permeate with a boron content less than 1 mg/L at recovery levels of up to 80%. This permeate can be then discarded into the environment or reused. The retentate that contains monoborate, mono- and dichelate boron complexes should be concentrated further in a second RO step, until it turns out to be possible to separate boron from it. It can be separated in the form of boric acid, since it is much less soluble than monoborate and boron complexes. This can be achieved by decomposition of monoborate and boron complexes with a strong mineral acid, such as HCl. Acidic post-crystallization lyes containing boric acid, alcohol and mineral salts can be then recycled to the ED demineralization step. An attempt to predict the effectiveness and costs of the above process was the objective of the presented paper.

2. The objective

The objective of this work was to propose a concept for an integrated ED–RO process for boron removal with simultaneous recovery in the form of boric acid. The effectiveness of this process was predicted based on the existing literature reports and by conducting the necessary experiments. In the proposed process, acidic (pH ≈ 3) boron–D-mannitol mixtures that contain salts are first desalinated by means of ED. This results in a demineralized diluate with all the alcohol and boron, and a concentrate with the majority of the salts and boron at less than 1 mg/L concentration. It should be emphasized that the sole purpose of ED in the proposed system is to remove ionic salts before RO treatment while the actual boron removal and concentration take part by RO. Such an integration of ED with RO allows the mitigation of osmotic pressure and inorganic scaling limitations during RO boron removal and concentration. After pH adjustment to more than 10.0, the diluate that contains mainly mono- and dichelate boron complexes is obtained. This mixture is concentrated in a two-stage RO system. In the first stage a permeate with a boron content less than 1 mg/L is obtained with recovery in excess of 80%. Due to its low boron content, the 1st stage permeate can be discarded to the environment or reused. The retentate obtained in the 1st stage is then concentrated in the 2nd RO stage until total boron concentration reaches the level of around 1 mol/L or more. The permeate from the 2nd RO stage contains excessive amounts of boron (>1 mg/L) therefore it needs to be recycled to the first stage. The 2nd stage retentate, in turn, is neutralized and slightly acidified with a strong mineral acid, e.g. concentrated HCl. This results in decomposition of boron–alcohol complexes and the precipitation of solid boric acid. Boric acid crystals are then filtered and the mother liquor is recycled back to the ED desalination step. The extent of D-mannitol transport across ED membranes at low pHs, and its transport across RO membranes at high pHs was shown to be small [8,13]. Therefore, it was assumed that the majority of alcohol will just circulate between the individual steps of the proposed system. If necessary, its concentration in the circulating loop can be adjusted by dissolving required amounts of solid D-mannitol in the post-crystallization lyes. The concept of the proposed process is schematically presented in Fig. 2.

Boron-rich leachate originating from the Tarnowskie Góry (Poland) chemical landfill storage facility, described previously in [9], was taken as an exemplary boron-rich water. The leachate in question contained 75 mg/L of boron and its TDS equaled 1.8 g/L. The effectiveness of the proposed system was predicted based on the results of numerical calculations. All the calculations conducted here were based on the existing literature data on boric acid, monoborate and boron complexes transport across membranes as well as the authors' experiment results.