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Heinonen Jari, Zhao Yan, Van der Bruggen Bart

This is a Final draft version of a publication  
published by Elsevier  
in Separation and Purification Technology

**DOI:** 10.1016/j.seppur.2020.116642

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**Please cite the publication as follows:**

Heinonen, J., Zhao, Y., Van der Bruggen, B. (2020). A process combination of ion exchange and electrodialysis for the recovery and purification of hydroxy acids from secondary sources. Separation and Purification Technology. DOI: 10.1016/j.seppur.2020.116642

**This is a parallel published version of an original publication.  
This version can differ from the original published article.**

**A PROCESS COMBINATION OF ION EXCHANGE AND  
ELECTRODIALYSIS FOR THE RECOVERY AND PURIFICATION  
OF HYDROXY ACIDS FROM SECONDARY SOURCES**

Jari Heinonen<sup>1,\*</sup>, Yan Zhao<sup>2</sup>, and Bart Van der Bruggen<sup>2,3</sup>

<sup>1</sup>School of Engineering Science  
LUT University  
Yliopistonkatu 34, FIN-53850 Lappeenranta, Finland

<sup>2</sup>Department of Chemical Engineering  
KU Leuven  
Celestijnenlaan 200F, BE-3001 Leuven, Belgium

<sup>3</sup>Faculty of Engineering and the Built Environment  
Tshwane University of Technology  
Private Bag X680, Pretoria 0001, South Africa

\*Corresponding author. Tel: +358-40-127 2920, e-mail: jari.heinonen@lut.fi

## ABSTRACT

Ion exchange and electrodialysis processes for the production of hydroxy acids (HAs) from alkaline soda and kraft black liquors (BLs) were investigated. Ion exchange with a type-2 strong anion exchange resin in sulfate form was used to separate thiosulfate from alkaline kraft-BL-based mixture of  $\text{Na}^+$  salts of HAs. Efficient regeneration of the spent resin to sulfate form was achieved only through hydroxide form. Ion exchange with strong cation exchange (SAC) resins was successfully used to convert the  $\text{Na}^+$  salts of HAs in soda-BL-based solution and thiosulfate-free kraft-BL-based solution into free acids with complete removal of  $\text{Na}^+$  ions from the solution. The spent resin was efficiently regenerated with 1–2 mol/L  $\text{H}_2\text{SO}_4$ . Electrodialysis with bipolar membranes (EDBM) was used for the generation of  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  from the spent SAC resin regenerants ( $\text{Na}_2\text{SO}_4$ – $\text{H}_2\text{SO}_4$  mixtures). Overall, 1 mol/L  $\text{H}_2\text{SO}_4$  with 95% purity and 90% yield could be obtained, but excess water flux through the membranes limited the maximum obtainable  $\text{H}_2\text{SO}_4$  concentration to 1.17 mol/L. Simultaneously, 0.79 mol/L  $\text{NaOH}$  was produced with 93% purity. EDBM-based  $\text{H}_2\text{SO}_4$  was successfully used for the regeneration of the SAC resin. With EDBM, a closed loop can be built for the regeneration of SAC resin with the simultaneous generation of  $\text{NaOH}$ . The results of this study demonstrate that a process combination of ion exchange and electrodialysis decreases the overall chemical consumption related to HA production and enables efficient chemical recycling.

Keywords: black liquor; hydroxy carboxylic acid; ion exchange; electrodialysis; bipolar membranes.

## 1 Introduction

Alkaline spent pulping liquors (black liquors, BLs), are formed during the chemical pulping of lignocellulosic materials. These contain hydroxy carboxylic acids (HAs), valuable platform chemicals that can be used for the production of fine chemicals [1–3], biodegradable polymers, and plastics [3–6], in tissue engineering [7], cosmetics [3,8,9], and the food industry [3], and as metal chelating agents [10–13]. Annually approximately 200 Mt (dry solids) of BLs are produced worldwide [14,15]. Of this, 20% is HAs and 10% formic acid (FA) and acetic acid (AA). BLs contain close to 100 HAs, and glycolic acid (GA), lactic acid (LA), glucoisosaccharinic acids (GISAs), xyloisosaccharinic acid (XISA), 2,5-dihydroxypentanoic acid (2,5-DHPA), and 2-hydroxybutanoic acid (2-HBA) are the main HAs [16–18].

Recently, chromatography-based methods for the production of pure mixtures of HAs with simultaneous recycling of lignin and spent pulping chemicals [19] and pure individual HAs [20] have been presented. HAs are present in BLs as sodium ( $\text{Na}^+$ ) salts, and although HA mixtures can be produced with the HAs in salt form [19], the production of pure individual HAs requires the HAs to be free acids (in  $\text{H}^+$  form) [20]. Thus, the HAs should be liberated.

HA liberation can be achieved by acidification with a mineral acid, but this does not remove  $\text{Na}^+$  ions from the solution, and the chemical consumption is high. Instead, ion exchange with a cation exchange resin in the  $\text{H}^+$  form could be used because this simultaneously removes the  $\text{Na}^+$  ions. However, this approach has not been investigated in detail prior to this study with both soda and kraft-BL-based solutions.

With soda BL, HA liberation by ion exchange can be carried out after the separation of lignin and  $\text{NaOH}$  [19,21]. However, this is not possible with kraft BL because of the presence of sodium

thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), which decomposes to elemental sulfur and sulfur dioxide under acidic conditions [19]. Sulfur, especially, is problematic as it would precipitate into the resin pores and, thus, render it as waste. In [19], the removal of  $\text{S}_2\text{O}_3^{2-}$  was achieved by acidification, but, as mentioned, this process is characterized by high chemical consumption as the chemicals cannot be recycled. Thus, alternatives should be found.

After HA liberation, the cation exchange resin must be regenerated. This can be done using  $\text{H}_2\text{SO}_4$ , which is already present in the pulp mills (e.g. [22]). The regeneration generates  $\text{Na}_2\text{SO}_4$  waste, which has little use and cannot be fed into the pulping process because it would disturb the Na/S balance of the process [23,24]. Electrodialysis with bipolar membranes (EDBM) could be used to convert the  $\text{Na}_2\text{SO}_4$  waste into  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . This is a textbook example of EDBM and has been studied to large extent (e.g. [25–28]). Raucq et al. [25] produced 0.25 L of 4 mol/L  $\text{NaOH}$  and 3.5 mol/L  $\text{H}_2\text{SO}_4$  with 95% purities from 2 L of 1 mol/L  $\text{Na}_2\text{SO}_4$ . Wei et al. [26] showed that for the production of  $\text{NaOH}$  from  $\text{Na}_2\text{SO}_4$ , low energy consumption and high current efficiency were achieved with 0.20–0.30 mol/L feed concentration, 0.10–0.25 mol/L initial base product concentration, and 30–60  $\text{mA}/\text{cm}^2$  current density [26]. Paleologou et al. [27] demonstrated that in the generation of  $\text{NaOH}$  with continuous product withdrawal constant  $\text{NaOH}$  concentration could be maintained with 1 mol/L initial  $\text{NaOH}$  concentration. Tran et al. [28] investigated an integrated system of a fluidized pellet reactor and EDBM for the regeneration of acid and base from sulfate and chloride-rich wastewater with a high concentration of calcium and nickel ions. After removal of the metal ions from the feed by crystallization in the fluidized pellet reactor, acid and base up to 1.76 and 2.41 N, respectively, were produced with only slight scaling of the membranes [28]. Although EDBM with  $\text{Na}_2\text{SO}_4$  as feed has been studied extensively, none of the

studies has involved feeds containing  $\text{H}_2\text{SO}_4$  in addition to  $\text{Na}_2\text{SO}_4$ , which would be the case with spent regenerant from the SAC resin used in HA liberation.

In this paper, we present an experimental study of ion exchange and electro dialysis processes that enable the resource efficient production of pure HAs from soda and kraft BLs (Fig. 1).  $\text{S}_2\text{O}_3^{2-}$  removal from kraft BL by anion exchange, HA liberation by cation exchange, and treatment of  $\text{Na}_2\text{SO}_4$ -rich spent cation exchange resin regenerant by EDBM are investigated. These enable the recycling of chemicals used in the production of HAs and in the pulping process, thus, increasing the economic feasibility of HA production. Optimization of these unit operations was not attempted.

<<Figure 1 around here>>

## **2 Materials and methods**

### **2.1 Chemicals and separation materials**

Ultrapure water,  $\text{Na}_2\text{SO}_4$  (98.5–101.0%, VWR),  $\text{NaOH}$  ( $\geq 99.0\%$ , pellets for analysis, Merck KGaA),  $\text{H}_2\text{SO}_4$  (95–97%, Merck KGaA),  $\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$  (99%, VWR),  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  ( $\geq 99\%$ , Merck KGaA),  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\geq 96\%$ , Merck KGaA),  $\text{CuSO}_4$  ( $\geq 99\%$ , Merck KGaA),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ( $\geq 99\%$ , Merck KGaA),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  ( $\geq 99\%$ , Merck KGaA), and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  ( $\geq 98\%$ , Merck KGaA) were used.

Commercially available chemicals were used as standards for the HAs [19,20]. Mixtures of  $\text{Na}^+$  salts of HAs (Table 1) were obtained from hardwood soda and kraft BLs using the method described in [19]. These solutions were not acidified (cf. [19]) and thus, the pH of the soda and

kraft BL-based solutions were 9.10 and 10.25, respectively. The ion exchange resins (Table 2) were converted to the correct ionic form using standard methods. The cation exchange (FKB-PK-130), anion exchange (FAB-PK-130), and bipolar (FBM) membranes (Table 3) were obtained from Fumatech GmbH.

<<Table 1 around here>>

<<Table 2 around here>>

<<Table 3 around here>>

## 2.2 Ion exchange studies

The ion exchange unit consisted of two two-piston pumps attached to a glass column with water heating jacket via a fluid degasser and an injection valve. A column with approximately 35 mL ( $d_{\text{bed}} = 1.5$  cm,  $h_{\text{bed}} = 20$  cm) bed volume (BV) was used. The column outlet stream was monitored by online conductivity, refractive index (RI), and ultraviolet (UV) detectors. A fraction collector was also connected to the column outlet. All experiments were carried out at 23 °C temperature.

### 2.2.1 Thiosulfate removal

Four SBA resins in the  $\text{OH}^-$  or  $\text{SO}_4^{2-}$  form were tested for the  $\text{S}_2\text{O}_3^{2-}$  removal from kraft-BL-based feed. Using SBA resins in the  $\text{OH}^-$  form (SBA resins; Table 2), one cycle (constant  $Q = 2$  BV/h) was carried out as follows. First, the feed was injected to the column until the online signals at column outlet were stabilized. Next, the excess feed was washed from the column with water (feed volume  $V^{\text{F}} = 3$  BV). The spent resin was regenerated to  $\text{OH}^-$  form with 2 mol/L NaOH ( $V^{\text{F}} = 3$  BV), and washed with water.

The type-2 SBA resin (AS542GC) was tested also in  $\text{SO}_4^{2-}$  form. The loading step and the subsequent washing step were carried out as with the  $\text{OH}^-$  form resins. In the regeneration, the resin was first converted to the  $\text{OH}^-$  form with 2 mol/L NaOH ( $V^F = 5$  BV), and washed with water ( $V^F = 3$  BV). Then, the resin was converted to  $\text{SO}_4^{2-}$  form with 1 mol/L  $\text{Na}_2\text{SO}_4$  ( $V^F = 4.33$  BV), and washed with water ( $V^F = 3$  BV).

### 2.2.2 HA liberation

Two gel-type SAC resins in  $\text{H}^+$  form were tested (Table 2). A pressure regulator valve with a 200 psi (13.8 bar) pressure rating was installed to the column outlet to prevent gas formation inside the column.

One cycle consisted of four steps (constant  $Q = 2$  BV/h). In the loading step,  $\text{S}_2\text{O}_3^{2-}$ -free mixtures of  $\text{Na}^+$  salts of HAs were fed to the column until the online detector signals were stabilized. Then the resin bed was washed with water ( $V^F = 3$  BV), and regenerated to the  $\text{H}^+$  form with  $\text{H}_2\text{SO}_4$ . Finally, the resin was washed with water ( $V^F = 3$  BV). The regeneration was carried out with 1–2 mol/L  $\text{H}_2\text{SO}_4$  solutions.

### 2.3 Electrodialysis with bipolar membranes

Generation of  $\text{H}_2\text{SO}_4$  and NaOH from the spent regenerant from HA liberation was studied using a laboratory-scale EDBM system PCCell ED 64-004 (PCCell GmbH) in batch mode with four cell triplets and an additional cation exchange membrane next to the anode (Fig. 2). The effective surface area of one membrane was  $64 \text{ cm}^2$ . The spacer thickness was 0.45 mm.



Feed, acid, and base solutions were circulated at a 20 L/h flowrate. 60 L/h flowrate was used for the electrode rinsing solution. A constant electrical potential difference of 16 V (generated with a DC power supply) was used.

Experiments were carried out with synthetic feed solutions (Table 4). Feed solutions free of multivalent cations were used in order to study the effect of feed  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  concentrations on the process performance. Feed solutions containing multivalent cations were used in order to monitor the scaling of the cation exchange membranes. The experiments were continued until the conductivity of the feed (monitored with an off-line conductivity meter) was close to zero. The acid and base compartments had 0.1 mol/L initial  $\text{H}_2\text{SO}_4$  and NaOH concentrations, respectively. 0.25 mol/L  $\text{Na}_2\text{SO}_4$  solution was used for electrode rinsing.

<<Table 4 around here>>

<<Figure 2 around here>>

## 2.4 Analyses

HAs were quantified according to previously reported methods [19,20], whereas residual lignin was quantified in basic solution according to [18] and in acidic solution according to TAPPI standard UM 250 [29]. Sodium was analyzed with an atomic absorption spectrometer (iCE 3000, Thermo Fisher Scientific) according to standards SFS 3044 and SFS 3017. Other metals were analyzed according to SFS ISO 17294-1 and SFS ISO 17294-2 standards with an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7900).  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  were analyzed by ion chromatography (IC; ICS-1100, Thermo Fisher) according to standard SFS-EN ISO 10304-2.

The column was an IonPac AG22 (4 × 50 mm + AS22 (4 × 250 mm)), and the eluent was 4.5 mmol/L Na<sub>2</sub>CO<sub>3</sub> with 1.4 mmol/L NaHCO<sub>3</sub>. Due to the use of alkaline eluent with IC, HSO<sub>4</sub><sup>-</sup> could not be detected as it dissociates into SO<sub>4</sub><sup>2-</sup> under alkaline conditions. Thus, the SO<sub>4</sub><sup>2-</sup> concentration obtained by ion chromatography for acidic samples also includes HSO<sub>4</sub><sup>-</sup>.

H<sub>2</sub>SO<sub>4</sub> and NaOH concentrations were determined by titration, and the pH was measured using an off-line pH meter (C3020 multiparameter analyzer (Consort bvba) with a Sentix Mic electrode (WTW)). Scanning electron microscope (SEM; SU3500, Hitachi) was used to analyze the scaling of the ion exchange membranes.

### **3 Results and discussion**

#### **3.1 Thiosulfate removal**

Four strong anion exchange resins in OH<sup>-</sup> form (Table 2) were tested (Fig. 3). The elution order of the compounds in the feed was qualitatively similar for each resin. Due to the ionic form of the resins, OH<sup>-</sup> ions in the feed were not taken up by the resin and thus, the breakthrough of these occurred after the void. With the 1X8 and AA16GC resins, the OH<sup>-</sup> profiles exhibited sharp front and rear parts (Fig. 3). This resulted in only a small overlapping of the OH<sup>-</sup> profile with those of the other compounds. With AS542GC and IRA-958 resins, OH<sup>-</sup> exhibited strong tailing and, thus, strong overlapping with the later eluting compounds (Fig. 3). The tailing is most probably mass transfer related in the case of AS542GC. Because the ionic form of this resin changes from OH<sup>-</sup> to a mixture of carboxylate and SO<sub>4</sub><sup>2-</sup> ions, the soft resin shrinks considerably, and the mass transfer rate of OH<sup>-</sup> from the resin to the bulk solution decreases, resulting in tailing. With the

other gel-type SBA resins, 1X8 and AA16GC, the tailing was absent, most likely because of the smaller resin volume changes: these resins have an 8 wt.% (DVB) nominal cross-linking degree, whereas that of AS542GC is 4 wt.%. With the macroporous IRA-958, the tailing might be due to the affinity between the  $\text{OH}^-$  and the acrylic matrix of the resin. Qualitatively similar, albeit stronger, tailing of  $\text{OH}^-$  has also been observed with acrylic weak cation exchange resins [19]; although this has been assumed to be due to the presence of two types of functional groups, our findings question that conclusion.

The second eluting compounds were the carboxylate ions of HAs (Fig. 3) because of the low selectivity of SBA resins towards these ions [30,31]. No separation of the individual  $\text{Na}^+$  salts of HAs was observed. This was expected because such separation has been accomplished only with free acids [20].

Unexpectedly,  $\text{SO}_4^{2-}$  ions co-eluted with the carboxylates (Fig. 3). Ion exchange resins are known to be substantially more selective towards divalent ions, such as  $\text{SO}_4^{2-}$ , than towards monovalent ions such as carboxylates or  $\text{OH}^-$  [31,32]. This co-elution is probably due to interactions between  $\text{SO}_4^{2-}$  and the carboxylate ions. Such interactions between acetate and sulfate species have been reported by other authors [33–35]. This is also not related to the BL-based feed because it was observed also with a synthetic solution containing  $\text{Na}^+$  salts of LA, FA, and AA,  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_2\text{S}_2\text{O}_3$  (see Supplementary Material). The co-elution of the  $\text{Na}^+$  salts of HAs and  $\text{SO}_4^{2-}$  prevents their separation by anion exchange. However, this can be achieved by electrolyte exclusion chromatography (EEC) after  $\text{Na}^+$  removal as was demonstrated in [19].

With 1X8 and AA16GC, the front of the  $\text{SO}_4^{2-}$  profile was sharper than the front of the HA profile (Fig. 3). In addition, overshoots in the  $\text{SO}_4^{2-}$  profile front, because of displacement, were observed.

The displacer, however, could not be identified because of analytical limitations. This was not caused by the HAs because it was not seen with the synthetic solution (see Supplementary Material). The displacer is most likely  $\text{CO}_3^{2-}$  ion, which is also present in BLs. Such overshoots were not observed with the AS542GC or IRA-958 (Fig. 3).

Each resin was most selective for  $\text{S}_2\text{O}_3^{2-}$  (Fig. 3), but there were clear differences in the dynamic capacities. 1X8 and AA16GC had approximately similar capacities (breakthrough at appr. 2.5 BV) for  $\text{S}_2\text{O}_3^{2-}$ . With IRA-958 the  $\text{S}_2\text{O}_3^{2-}$  breakthrough occurred roughly after 1 BV whereas with AS542GC the breakthrough occurred after 3.2 BV. The good capacity of AS542GC for  $\text{S}_2\text{O}_3^{2-}$  was unexpected because type-2 resins generally have smaller selectivity differences between  $\text{OH}^-$  and other ions than type-1 SBA resins [30,31]. No overshoots for  $\text{SO}_4^{2-}$  or the carboxylates arising from displacement at the front of the  $\text{S}_2\text{O}_3^{2-}$  profile were observed.

The feed solution also contained a small amount of residual lignin (see Table 1). The color of each SBA resin changed to dark brown because of the lignin compounds (data not shown). The color could not be removed from the resins during regeneration with 2 mol/L NaOH.

<<Figure 3 around here>>

Regeneration of the SBA resins from  $\text{S}_2\text{O}_3^{2-}$  form to  $\text{OH}^-$  form was tested with 2 mol/L NaOH (Fig. 3, Table 5). Only a fraction of the  $\text{S}_2\text{O}_3^{2-}$  taken up by the 1X8 and AA16GC resins could be eluted. In addition, strong tailing of  $\text{S}_2\text{O}_3^{2-}$  was observed (Fig. 3). Thus, although these resins have good capacity and selectivity for  $\text{S}_2\text{O}_3^{2-}$ , these cannot be recommended to be used for the  $\text{S}_2\text{O}_3^{2-}$  removal due to the low regeneration efficiency.

<<Table 5 around here>>

Complete elution of  $\text{S}_2\text{O}_3^{2-}$  could be accomplished with AS542GC and IRA-958 (Table 5). However, the dynamic capacity of IRA-958 for  $\text{S}_2\text{O}_3^{2-}$  was approximately 80% lower than that of AS542GC. Thus, only AS542GC was found to be suitable for  $\text{S}_2\text{O}_3^{2-}$  removal. However, as  $\text{OH}^-$  exhibited long tailing with this resin during the loading step (Fig. 3), the resulting fraction of  $\text{Na}^+$  salts of HAs would contain a high amount of NaOH. This is not feasible because NaOH has been separated from the HA feed in the previous process step (cf. [19]).

Because of the high capacity for  $\text{S}_2\text{O}_3^{2-}$  and low capacity for  $\text{SO}_4^{2-}$ , the AS542GC resin was also tested in  $\text{SO}_4^{2-}$  form for the  $\text{S}_2\text{O}_3^{2-}$  removal (Fig. 4). The elution order was similar to that of the resin in the  $\text{OH}^-$  form (Fig. 4).  $\text{SO}_4^{2-}$  eluted from the column at the void, and a very strong overshoot in the concentration was observed. The profile exhibited relatively strong tailing, but not as strong as  $\text{OH}^-$  with the resin in  $\text{OH}^-$  form (Fig. 3).

The carboxylates of the HAs eluted after  $\text{SO}_4^{2-}$  (Fig. 4), but with a more dispersed front when compared to the resin in  $\text{OH}^-$  form. The shapes of the  $\text{SO}_4^{2-}$  and HA profiles suggest that the HAs displace the  $\text{SO}_4^{2-}$  ions from the resin. This is completely opposite to the behavior expected on basis of the selectivity data from literature [30,31].

$\text{S}_2\text{O}_3^{2-}$  eluted last, with breakthrough occurring after 3.6 BV (Fig. 4), which is approximately 12% higher than with the resin in  $\text{OH}^-$  form. Overshoots for  $\text{SO}_4^{2-}$  or HAs at the front of the  $\text{S}_2\text{O}_3^{2-}$  profile were not observed. In addition, the resin did not take up  $\text{OH}^-$  ions strongly, and, thus, the pH reached the feed value quickly after the void (Fig. 4).

Regeneration of AS542GC to the  $\text{SO}_4^{2-}$  form was found to be more challenging than regeneration to the  $\text{OH}^-$  form. First, this was tested with 1 mol/L  $\text{Na}_2\text{SO}_4$ , but even after 8 BV, the outlet stream contained  $\text{S}_2\text{O}_3^{2-}$  (data not shown).  $\text{H}_2\text{SO}_4$  could not be used for regeneration because  $\text{S}_2\text{O}_3^{2-}$  decomposes under acidic conditions into elemental sulfur, which would precipitate into the pores of the resin.

The regeneration of AS542GC to the  $\text{SO}_4^{2-}$  form could be done in two steps (Fig. 4). First, the resin was converted into  $\text{OH}^-$  form using 2 mol/L  $\text{NaOH}$ . Simultaneously with  $\text{S}_2\text{O}_3^{2-}$ , residual  $\text{SO}_4^{2-}$  was removed (Fig. 4). The resin was then converted to  $\text{SO}_4^{2-}$  form with 1 mol/L  $\text{Na}_2\text{SO}_4$ .  $\text{H}_2\text{SO}_4$  could not be used because the resulting neutralization reaction would increase the temperature inside the resin and, thus, cause damage to the resin. Type-2 SBA resins are known to have a low thermal stability, especially in the  $\text{OH}^-$  form [32].

The color of AS542GC in  $\text{SO}_4^{2-}$  form changed to dark brown because of lignin residues, and the color could not be removed during the regeneration. However, preliminary tests indicated that the treatment of the resin in  $\text{SO}_4^{2-}$  form with  $\text{H}_2\text{SO}_4$  results in the disappearance of the color.

<<Figure 4 around here>>

The  $\text{S}_2\text{O}_3^{2-}$  removal was carried out for 10 cycles to monitor the process stability (see Supplementary Material). No notable changes in the efficiency were observed. Similar results were obtained in the chromatographic purification of lignocellulosic hydrolysates using a weak cation exchange resin [36,37]: although the resin color changed to dark brown because of lignin compounds, the separation efficiency was not affected. Evidently, 10 cycles is a rather short duration and a longer run should be used to properly evaluate this method.

As seen from above,  $S_2O_3^{2-}$  can be removed from kraft-BL-based mixtures of  $Na^+$  salts of HAs with a type-2 SBA resin in  $SO_4^{2-}$  form, but this does not remove  $SO_4^{2-}$  from the solution. For this, EEC can be used after the HA liberation step [19,38–40]. Thus, in this respect, the outcome is similar to the situation when  $S_2O_3^{2-}$  removed by acidification (cf. [19]). The advantage of the ion exchange treatment is the possibility of recycling chemicals, which significantly reduces chemical consumption. This applies also to  $S_2O_3^{2-}$ , which can be recycled as in normal pulp mill operation to the recovery boiler of the mill [21,24].

### 3.2 HA liberation

The liberation of HAs from soda-BL-based feeds was studied with two gel-type strong cation exchange resins (6 and 8 wt.% DVB; Table 2) in  $H^+$  form (Fig. 5). Qualitatively, the results obtained with both resins were similar. No separation between the individual HAs could be obtained with the SAC resins.

The point at which all the protons in the resins were exchanged by  $Na^+$  could be seen from the online conductivity signal (Fig. 5). As long as free HAs were eluted from the column, the conductivity signal was close to zero because of the low degree of dissociation under acidic conditions. When the resin was exhausted of  $H^+$ , the conductivity signal increased quickly with the elution of the fully dissociated  $Na^+$  salts of the HAs. As expected, a larger amount of the feed could be treated with CS16GC owing to the higher volumetric ion exchange capacity (Fig. 5). The breakthrough of  $Na^+$  ions with this resin occurred at 2.6 BV, which was approximately 10% larger than with CS12GC.

The feed solution contained approximately 42 g/L of HAs (the main HAs). This is equivalent to 0.41 mol/L  $\text{Na}^+$  ions, which means that breakthrough with CS16GC should have occurred at 4.7 BV instead of 2.6 BV. The feed  $\text{Na}^+$  concentration was actually 0.76 mol/L, which corresponds to a breakthrough volume of 2.54 BV. This is close to the obtained value. The additional  $\text{Na}^+$  ions originate from the other electrolytes in the feed, such as residual NaOH and  $\text{Na}_2\text{CO}_3$  (not quantified because of analytical limitations). However, the presence of  $\text{Na}_2\text{CO}_3$  was confirmed by the formation of  $\text{CO}_2$  during acidification of the soda-BL-based feed. The formation of  $\text{CO}_2$  inside the resin bed would result in the channeling of the fluid flow, and, thus, the ion exchange capacity could be only partially utilized. This was prevented by increasing the pressure inside the column with a pressure regulator valve.

The liberation of HAs from  $\text{S}_2\text{O}_3^{2-}$ -free kraft-BL-based mixtures of  $\text{Na}^+$  salts of HAs was carried out with CS16GC (Fig. 5). The feed contained approximately 44 g/L of HAs and 32.5 g/L  $\text{Na}_2\text{SO}_4$ . In this case, the resin was exhausted after 1.65 BV, which is 37% less than that with the soda-BL-based feed. This decrease is mainly due to  $\text{Na}_2\text{SO}_4$  because the amount of  $\text{Na}^+$  from the HAs (0.45 mol/L) was approximately the same as with the soda-BL-based feed. The amount of  $\text{Na}^+$  ions originating from the  $\text{Na}_2\text{SO}_4$  was approximately 0.46 mol/L. Based on these values, the breakthrough of  $\text{Na}^+$  should have occurred after 2.1 BV. However, this feed also contained  $\text{Na}_2\text{CO}_3$ , which further decreased the breakthrough volume.

<<Figure 5 around here>>

The regeneration of the spent CS16GC to  $\text{H}^+$  form was tested using 1–2 mol/L  $\text{H}_2\text{SO}_4$  with a resin that was loaded with an authentic soda-BL-based feed solution (Fig. 6). In each case, the resin was



successfully regenerated, and spent regenerants containing  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  were obtained (Table 4; Fig. 6). These solutions contained also multivalent cations originating from the soda-BL-based feed. However, no traces of lignin could be detected in these fractions.

<<Figure 6 around here>>

The volume of the regenerant decreased and the average product concentrations in the spent regenerant increased with increasing  $\text{H}_2\text{SO}_4$  concentration in the fresh regenerant. However, the ratios of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  were approximately the same in each case (see Table 4). The amount of 1.0 mol/L  $\text{H}_2\text{SO}_4$  needed to convert the resin fully to  $\text{H}^+$  form was 2.7 BV (0.36 BV resin bed void volume). With 2 mol/L  $\text{H}_2\text{SO}_4$ , the required volume was two times smaller. Thus, the use of a high  $\text{H}_2\text{SO}_4$  concentration would result in a significant decrease in the amount of process water needed.

### 3.3 Generation of $\text{H}_2\text{SO}_4$ and $\text{NaOH}$ by EDBM

The spent regenerants from HA liberation were treated by EDBM to generate  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . Because of the different scales of the ion exchange ( $V_{\text{bed}} = 35$  mL) and EDBM units ( $V_{\text{solution}} = 1.5$ –2 L), synthetic solutions were used. These had the same compositions as the authentic spent regenerants with respect to the quantified compounds (Table 4).

EDBM experiments with equal initial volumes of feed, acid product, and base product tanks (2 L) were carried out (Fig. 7; see Supplementary Material for current densities) with feed solutions

resulting from regeneration of the CS16GC resin with 1–2 mol/L  $\text{H}_2\text{SO}_4$  (Table 4). In these experiments, the feed did not contain multivalent cations.

In each case, the concentrations in the feed tank decreased similarly towards zero (Fig. 7 feed) because of the similar  $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$  ratios (Table 4) and identical experimental conditions. Initially, the  $\text{H}_2\text{SO}_4$  concentration decreased in the feed tank faster than the  $\text{Na}_2\text{SO}_4$  concentration, whereas, at the end, the opposite situation was observed (Fig. 7 feed). The differences in the concentration gradients can be explained by the different cations, i.e.,  $\text{H}^+$  and  $\text{Na}^+$ . The initially faster decrease in  $\text{H}_2\text{SO}_4$  is due to the higher  $\text{H}^+$  concentration and higher concentration difference between the feed and the base product tank. This results in a higher chemical potential difference and stronger driving force for the diffusion of  $\text{H}^+$  over  $\text{Na}^+$ . The higher concentration difference of  $\text{H}^+$  ions between the feed and base product tanks with respect to that of  $\text{Na}^+$  ions remained for the duration of the experiment because  $\text{H}^+$  ions that enter the base product tank are consumed by the neutralization reaction with  $\text{OH}^-$  ions from the bipolar membrane. However, after a certain time (approximately 500 min with feed A), the reduction in the concentration of  $\text{Na}_2\text{SO}_4$  becomes faster than that of  $\text{H}_2\text{SO}_4$ . This is because cation exchangers are generally more selective towards  $\text{Na}^+$  over  $\text{H}^+$  [32], which is also assumed to be the case here; therefore, even though there is a higher  $\text{H}^+$  difference over the anion exchange membrane, the  $\text{Na}^+$  ions diffuse faster to the base product tank when the  $\text{H}^+$  concentration is sufficiently low.

In the acid product tank,  $\text{H}_2\text{SO}_4$  is formed from  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  (these were not detected due to analytical limitations) ions diffusing through the anion exchange membrane from the feed tank and from  $\text{H}^+$  from the bipolar membrane. The  $\text{H}_2\text{SO}_4$  concentration increased rather linearly while sufficient  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  ions were available in the feed tank (Fig. 7 acid). However, after a certain point the water flux through the membrane became so large that the increase levelled off.

With feeds A and B, the rate of increase of the  $\text{H}_2\text{SO}_4$  concentration was found to depend strongly on the initial feed concentration (Fig. 7 acid): a higher feed concentration resulted in a greater increase. This is due to the higher electrical conductivity over the EDBM stack. However, the target  $\text{H}_2\text{SO}_4$  concentrations of 1 and 1.5 mol/L could not be reached with feeds A and B, respectively (Fig. 7 acid). This was because the initial  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  concentrations in the feed were lower than the target value. For example, feed A initially contained 0.94 mol/L these compounds, and, thus, 1.04 mol/L is the theoretical maximum  $\text{H}_2\text{SO}_4$  concentration when the initial 0.1 mol/L  $\text{H}_2\text{SO}_4$  concentration in the acid product tank is taken into account. However, the actual concentration was decreased by the migration of  $\text{HSO}_4^-$  (which dissociates fully to  $\text{SO}_4^{2-}$  in alkaline conditions) and  $\text{SO}_4^{2-}$  ions to the base product tank (Fig. 7 base) and water flux.

In the case of feed A, the final  $\text{H}_2\text{SO}_4$  concentration was approximately 80% of the target value, whereas that of feed B was approximately 77%. The slightly lower value with feed B resulted from the higher water flux through the anion exchange membrane because of the higher concentration difference between the feed and acid product tanks.

With feed C, the final  $\text{H}_2\text{SO}_4$  concentration was even lower than with feed B (Fig. 7 acid): the final concentration was only 56% of the target value. This indicates that feed C was too concentrated for the EDBM system. Quantitatively, the results were similar to those with feeds A and B, but the water flux to the acid product tank was considerably higher. The volume of the acid product tank increased by 230 mL during the experiment, and this value is 3.6 times higher than that with feed A.

$\text{Na}^+$  ions also migrated to the acid product tank and their concentration increased continuously (Fig. 7 acid). This resulted in a decrease in the purity of the acid product. In the final product, the  $\text{H}_2\text{SO}_4$  purity was 95.1% with feeds A and B, but only 90% with feed C.

The behavior of NaOH in the base product tank was qualitatively similar to that of  $\text{H}_2\text{SO}_4$  in the acid product tank for the same reasons (Fig. 7 base). The NaOH concentration that could be obtained with feed A was 0.65 mol/L, which was approximately 74% of the theoretical value with 0.1 mol/L initial NaOH concentration in the base product tank. With feed B, the final concentration was 71% of the theoretical value ( $C_{\text{theor}} = 1.12$  mol/L) and, with feed C, it was 56% ( $C_{\text{theor}} = 1.42$  mol/L). The NaOH concentrations were lower than the theoretical values because of the migration of  $\text{Na}^+$  to the acid product tank and water flux.

Migration of  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  ions from the feed to the base product tank (Fig. 7 base) resulted in a decrease in product purity. The purities were 93%, 87%, and 82% for feeds A, B, and C, respectively. In contrast with the  $\text{H}_2\text{SO}_4$ , the NaOH purity was different for each feed.

<<Figure 7 around here>>

To reach the target  $\text{H}_2\text{SO}_4$  concentration, the initial volumes of the acid and base product tanks were reduced from 2 to 1.5 L (Fig. 8; see Supplementary Material for current densities). Feeds A and B containing only  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  were used. As expected, the results (Fig. 8) were qualitatively similar to those obtained with 2 L initial volumes (Fig. 7). Because similar feeds were used in both sets of experiments, the concentration gradients in the feed tanks were identical.

However, because of the lower initial volumes in the product tanks, the concentration gradients in these tanks were steeper than those with the 2 L initial volumes.

With feed A, the 1 mol/L target for H<sub>2</sub>SO<sub>4</sub> was reached (Fig. 8 acid). The water flux through the membranes to the acid product tank prevented obtaining higher H<sub>2</sub>SO<sub>4</sub> concentration with feed A. With feed B, only 1.17 mol/L H<sub>2</sub>SO<sub>4</sub> concentration could be reached. This is approximately the same value as obtained with feed C with the 2 L initial volumes (see Fig. 7 acid). Thus, 1.17 mol/L is the maximum H<sub>2</sub>SO<sub>4</sub> concentration that can be obtained with the EDBM setup in question. The H<sub>2</sub>SO<sub>4</sub> purities with feed A and B were 95% and 90%, respectively. The feed A purity was similar to that of the 2 L initial volume, but the feed B purity was 5% lower. These results are acceptable as the regeneration of the SAC resin can be achieved with 1 mol/L H<sub>2</sub>SO<sub>4</sub>. The use of less concentrated H<sub>2</sub>SO<sub>4</sub> is also better for membrane and resin stability in the long term.

The decrease in the initial volume of the base product tank resulted in an increase in the NaOH concentration when compared to the values obtained with 2 L initial volume (Fig. 8). With feeds A and B, the final NaOH concentrations were 0.82 mol/L and 1.05 mol, which were 72% and 66% of the theoretical values, respectively. The purities of the NaOH products were 93% and 88%, respectively. These values were similar to those obtained with the 2 L initial volumes.

The authentic spent regenerants from HA liberation also contain multivalent cations (Table 4) that form slightly soluble hydroxides under basic conditions. These could result in scaling of the cation exchange membranes [28,41]. This tendency was studied with synthetic feed solutions containing all the ions quantified in the authentic solutions (Table 4; Fig. 8).

The EDBM performance was unaffected by the multivalent ions (Fig. 8). The concentrations of the multivalent ions decreased only slightly over the major part of the experiments. This is due to

the low concentration of these ions in the feed, which results in a weak driving force for migration through the membrane even though cation exchangers are generally more selective for multivalent cations. Only when the total concentrations of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  decreased below 0.3 mol/L did the concentration of multivalent ions begin to decrease because of the migration to the base product (Fig. 8).

The membrane scaling caused by hydroxide precipitates was studied by SEM (Fig. 9). Some scaling was found on the base product sides of the cation exchange membranes. Although the cation exchange membranes are also in contact with the feed, no scaling on this side of the membranes was observed, unlike in other studies (cf. [28]). This was because of the low feed pH, which prevented the formation of hydroxides even when  $\text{OH}^-$  ions leak from the base side to the feed side of the cation exchange membranes.

With feed A, 89.6%  $\text{H}_2\text{SO}_4$  yield could be obtained, and the remainder formed  $\text{Na}_2\text{SO}_4$  in the acid product (4.8%), and  $\text{Na}_2\text{SO}_4$  in the base product (5.6%). If 1.56  $\text{Na}^+/\text{H}^+$  selectivity [30] is used for the CS16GC resin, after regeneration of the resin with 89.6% of recycled regenerant (1 mol/L  $\text{H}_2\text{SO}_4$ ;  $Pu = 95\%$ ) and 10.4% of fresh 1 mol/L  $\text{H}_2\text{SO}_4$ , 97% of the resin bed should be in  $\text{H}^+$  form. Thus, the  $\text{Na}_2\text{SO}_4$  impurity in the recycled regenerant will only result in a slight decrease in the resin capacity. This was confirmed with the kraft-BL-based mixture of  $\text{Na}^+$  salts of HAs (Fig. 5). Fresh CS16GC resin fully in the  $\text{H}^+$  form was loaded with this feed and then regenerated with a synthetic 1 mol/L  $\text{H}_2\text{SO}_4$  solution mimicking that obtained by EDBM. Finally, the resin was loaded again with the kraft-BL-based feed (Fig. 5). The breakthrough of  $\text{Na}^+$  occurred at approximately 1.61 BV, which is only 2% earlier than that in the case of the fresh resin.

These results demonstrate that the  $\text{Na}_2\text{SO}_4$  waste from HA liberation can be converted efficiently to  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  by EDBM. The generated  $\text{H}_2\text{SO}_4$  can be used for the regeneration of the SAC resin. However, due to less than 100%  $\text{H}_2\text{SO}_4$  yield in EDBM, some fresh  $\text{H}_2\text{SO}_4$  is also required.  $\text{NaOH}$  obtained by EDBM can be used in the SBA resin regeneration or the pulping process.

<<Figure 8 around here>>

<<Figure 9 around here>>

#### **4 Conclusions**

Use of ion exchange and electrodialysis processes for the production of HAs from soda and kraft BL were investigated. The studied unit operations were the  $\text{S}_2\text{O}_3^{2-}$  removal from kraft BL by anion exchange, the conversion of  $\text{Na}^+$  salts of HAs into free acids by cation exchange, and the generation of  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  from spent cation exchange resin regenerant by EDBM.

With kraft BL, the  $\text{S}_2\text{O}_3^{2-}$  removal must be carried out before HA liberation. This can be accomplished efficiently by ion exchange with a type-2 strong anion exchange resin in  $\text{SO}_4^{2-}$  form. Regeneration of the spent resin requires the use of both  $\text{NaOH}$  and  $\text{Na}_2\text{SO}_4$ . Although the regeneration is challenging, this method enables efficient recycling of the chemicals.

The conversion of the  $\text{Na}^+$  salts of HAs to free acids can be efficiently achieved with a strong cation exchange resin in  $\text{H}^+$  form. The regeneration of the spent resin to  $\text{H}^+$  form can be done with  $\text{H}_2\text{SO}_4$ . This generates a  $\text{Na}_2\text{SO}_4$ -rich waste solution that can be treated with EDBM to generate  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . This  $\text{H}_2\text{SO}_4$  can be used in cation exchange resin regeneration. The  $\text{NaOH}$  can be used for the regeneration of the anion exchange resin used in  $\text{S}_2\text{O}_3^{2-}$  removal or in the pulping process.

By using a combination of ion exchange and electro dialysis processes, the resource efficiency of HA production from secondary sources can be increased because the chemicals can be recycled for the HA production or pulping processes, and generation of chemical waste is minimized.

### **Acknowledgements**

Financial support from the Academy of Finland (grant SA/298548) is gratefully acknowledged.

The authors would like to express their thanks to Dr. Maaret Paakkunainen, Mr. Toni Väkiparta, Ms. Christine Wouters, and Ms. Michéle Vanroelen for their help with the analyses.

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## **SUPPLEMENTARY MATERIAL**

<<Figure A1 here>>

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## FIGURE CAPTIONS

- Figure 1. Ion exchange and EDBM processes for the production of HAs.
- Figure 2. Stack configuration in the EDBM.
- Figure 3. Removal of  $\text{S}_2\text{O}_3^{2-}$  by SBA resins in  $\text{OH}^-$  form in a column. Experimental conditions:  $Q = 2$  BV/h;  $T = 23$  °C;  $h_{\text{bed}} = 20$  cm;  $d_{\text{bed}} = 1.5$  cm; regenerant = 2 mol/L NaOH. Symbols: black circles =  $\text{SO}_4^{2-}$ ; green triangles =  $\text{S}_2\text{O}_3^{2-}$ ; red squares = HAs; blue diamonds = pH. Dark pink lines = electrical conductivity.
- Figure 4. Removal of  $\text{S}_2\text{O}_3^{2-}$  from kraft-BL-based mixture of  $\text{Na}^+$  salts of HAs with type-2 SBA resin AS542GC in  $\text{SO}_4^{2-}$  form in a column. Experimental conditions:  $h_{\text{bed}} = 20$  cm. For other details, see caption to Fig. 3.
- Figure 5. Liberation of HAs in BL-based mixtures of  $\text{Na}^+$  salts of HAs with gel-type SAC resins in  $\text{H}^+$  form in a column. Experimental conditions:  $h_{\text{bed}} = 20$  cm;  $Q = 2$  BV/h;  $T = 23$  °C. Symbols: grey downward triangles =  $\text{Na}^+$ . For other details, see caption to Fig. 3.
- Figure 6. Regeneration of 8 wt.% cross-linked gel-type SAC resin in a column. Experimental conditions:  $h_{\text{bed}} = 20$  cm;  $Q = 2$  BV/h;  $T = 23$  °C. Symbols: cyan circles =  $\text{H}^+$ . For other details, see caption to Fig. 3. Black dashed lines = cut-points for the fraction of spent regenerant.
- Figure 7. Generation of  $\text{H}_2\text{SO}_4$  and NaOH from  $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{SO}_4$  mixtures by EDBM. Experimental conditions:  $\Delta\phi = 16$  V;  $Q^{\text{FEED}} = Q^{\text{ACID}} = Q^{\text{BASE}} = 20$  L/h;  $Q^{\text{RINSE}} = 60$  L/h;  $V_{\text{initial}}^{\text{FEED}} = V_{\text{initial}}^{\text{ACID}} = V_{\text{initial}}^{\text{BASE}} = V_{\text{initial}}^{\text{RINSE}} = 2$  L; for other details, see Section 2.4. Feed solution: see Table 4. Symbols: squares =  $\text{H}_2\text{SO}_4$ ; circles =  $\text{Na}_2\text{SO}_4$ ; triangles = NaOH. Colors: target  $\text{H}_2\text{SO}_4$  concentration; black = 1 mol/L; red = 1.5 mol/L; blue = 2 mol/L.
- Figure 8. Generation of  $\text{H}_2\text{SO}_4$  and NaOH from  $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{SO}_4$  mixtures by EDBM. Experimental conditions:  $V_{\text{initial}}^{\text{FEED}} = V_{\text{initial}}^{\text{RINSE}} = 2$  L;  $V_{\text{initial}}^{\text{ACID}} = V_{\text{initial}}^{\text{BASE}} = 1.5$  L. Symbols: closed = without multivalent ions; open = with multivalent ions; diamond = trace metals. For other details, see caption to Fig. 7.
- Figure 9. SEM images of the scaling on the feed (A) and base product (B) sides of the cation exchange membranes used in the EDBM system.

- Figure A1. Separation of  $\text{S}_2\text{O}_3^{2-}$  by 1X8 resin in the  $\text{OH}^-$  form in the column. Feed composition: 48.8 g/L  $\text{Na}^+$  salts of HAs (given as free acids), 5.1 g/L  $\text{SO}_4^{2-}$ , and 7.5 g/L  $\text{S}_2\text{O}_3^{2-}$ . For other details, see caption of Fig. 3.
- Figure A2. Signal from online conductivity detector during the loading step in cyclic  $\text{S}_2\text{O}_3^{2-}$  separation runs. Colors: black = 1<sup>st</sup> cycle; green = 2<sup>nd</sup> cycle; dark pink = 4<sup>th</sup> cycle; blue = 6<sup>th</sup> cycle; cyan = 8<sup>th</sup> cycle; red = 10<sup>th</sup> cycle. For other details, see caption to Fig. 4.
- Figure A3. Current densities in EDBM experiments. Symbols: diamonds =  $V_{\text{initial}}^{\text{FEED}} = V_{\text{initial}}^{\text{ACID}} = V_{\text{initial}}^{\text{BASE}} = V_{\text{initial}}^{\text{RINSE}} = 2$  L; open squares =  $V_{\text{initial}}^{\text{FEED}} = V_{\text{initial}}^{\text{RINSE}} = 2$  L;  $V_{\text{initial}}^{\text{ACID}} = V_{\text{initial}}^{\text{BASE}} = 1.5$  L, no multivalent ions; circles =  $V_{\text{initial}}^{\text{FEED}} = V_{\text{initial}}^{\text{RINSE}} = 2$  L,  $V_{\text{initial}}^{\text{ACID}} = V_{\text{initial}}^{\text{BASE}} = 1.5$  L; with multivalent ions. Colors: see caption to Fig. 7.



**Lignin and NaOH free HA fraction from soda BL**

**Lignin and NaOH free HA fraction from kraft BL**

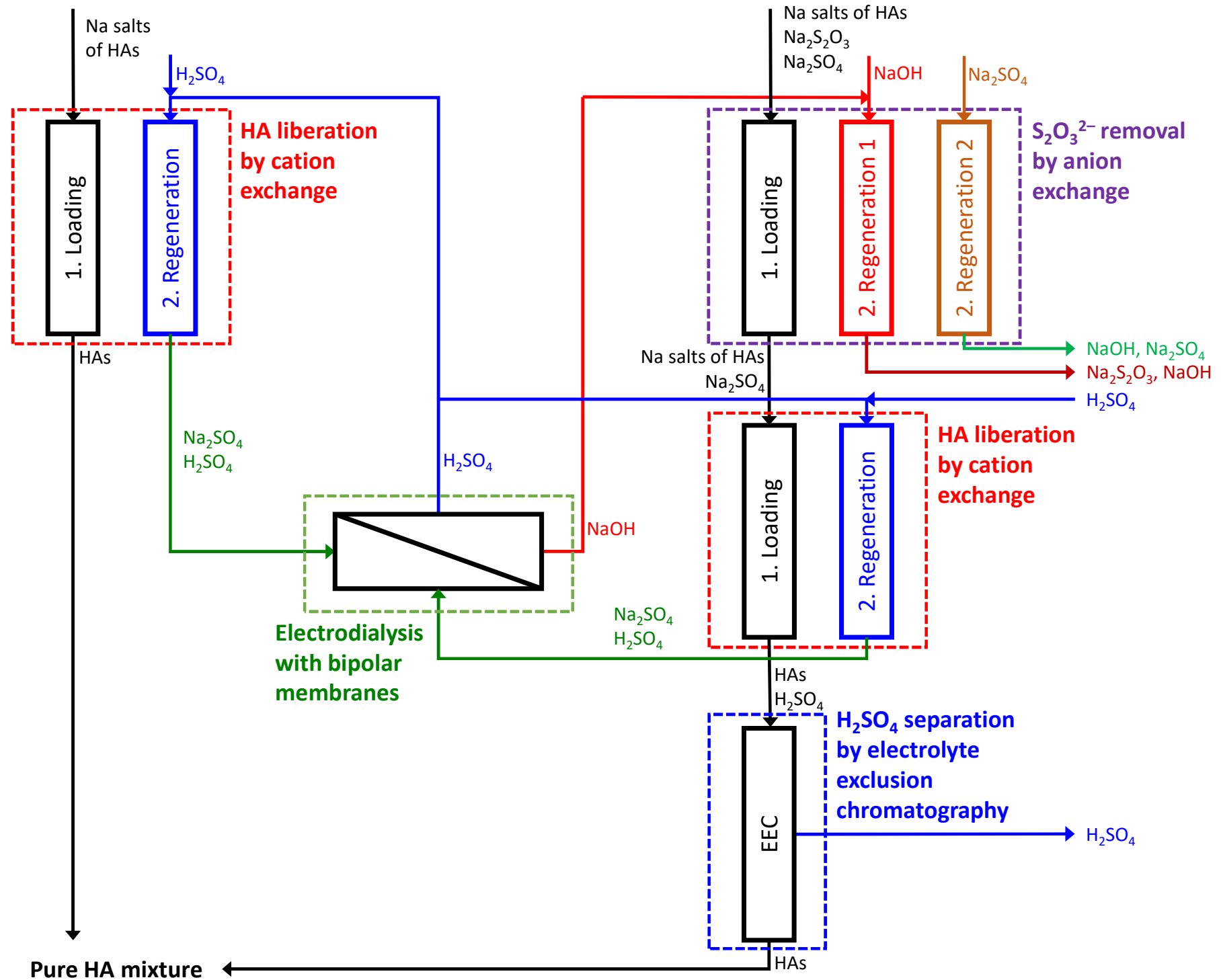


Figure 1

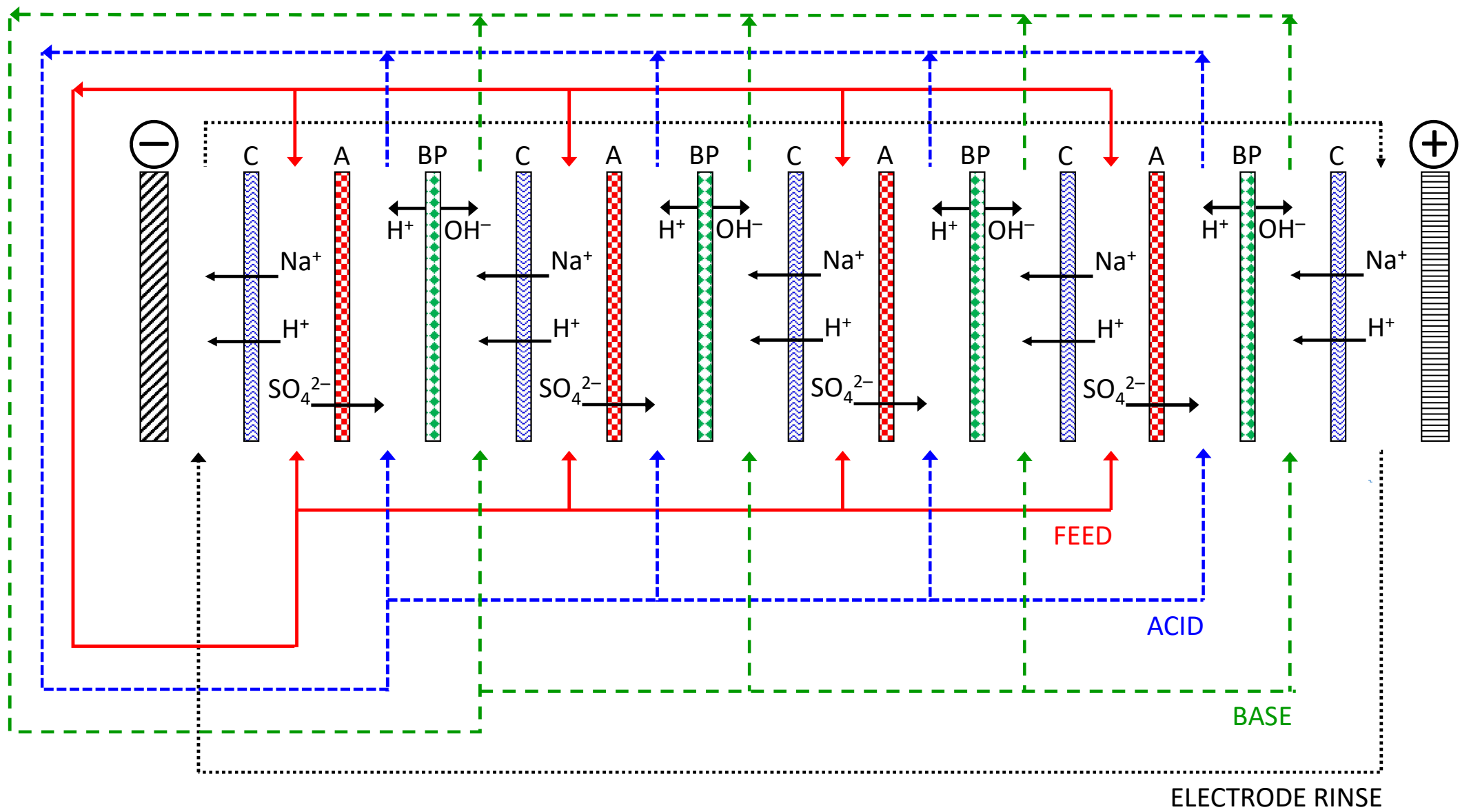


Figure 2

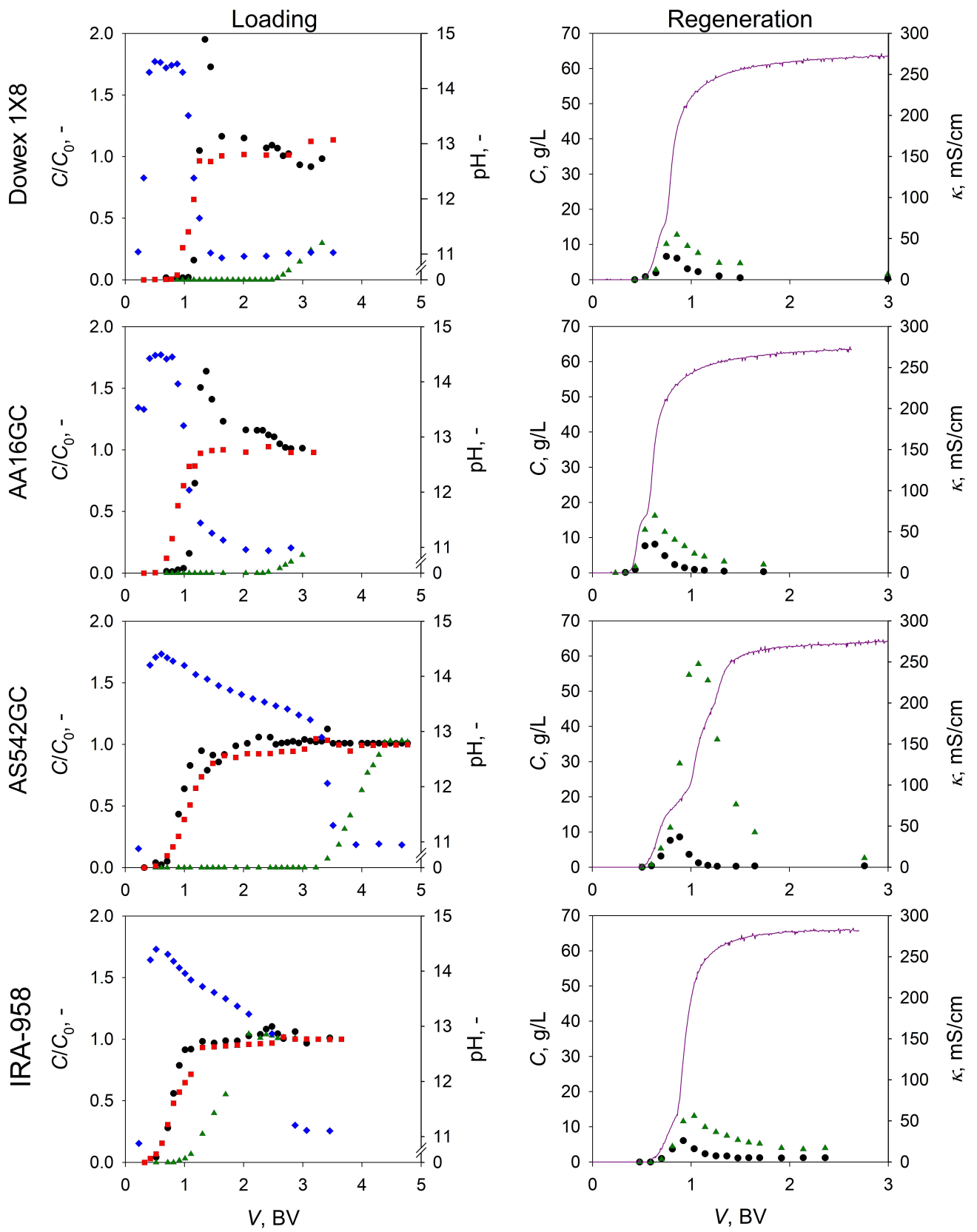


Figure 3

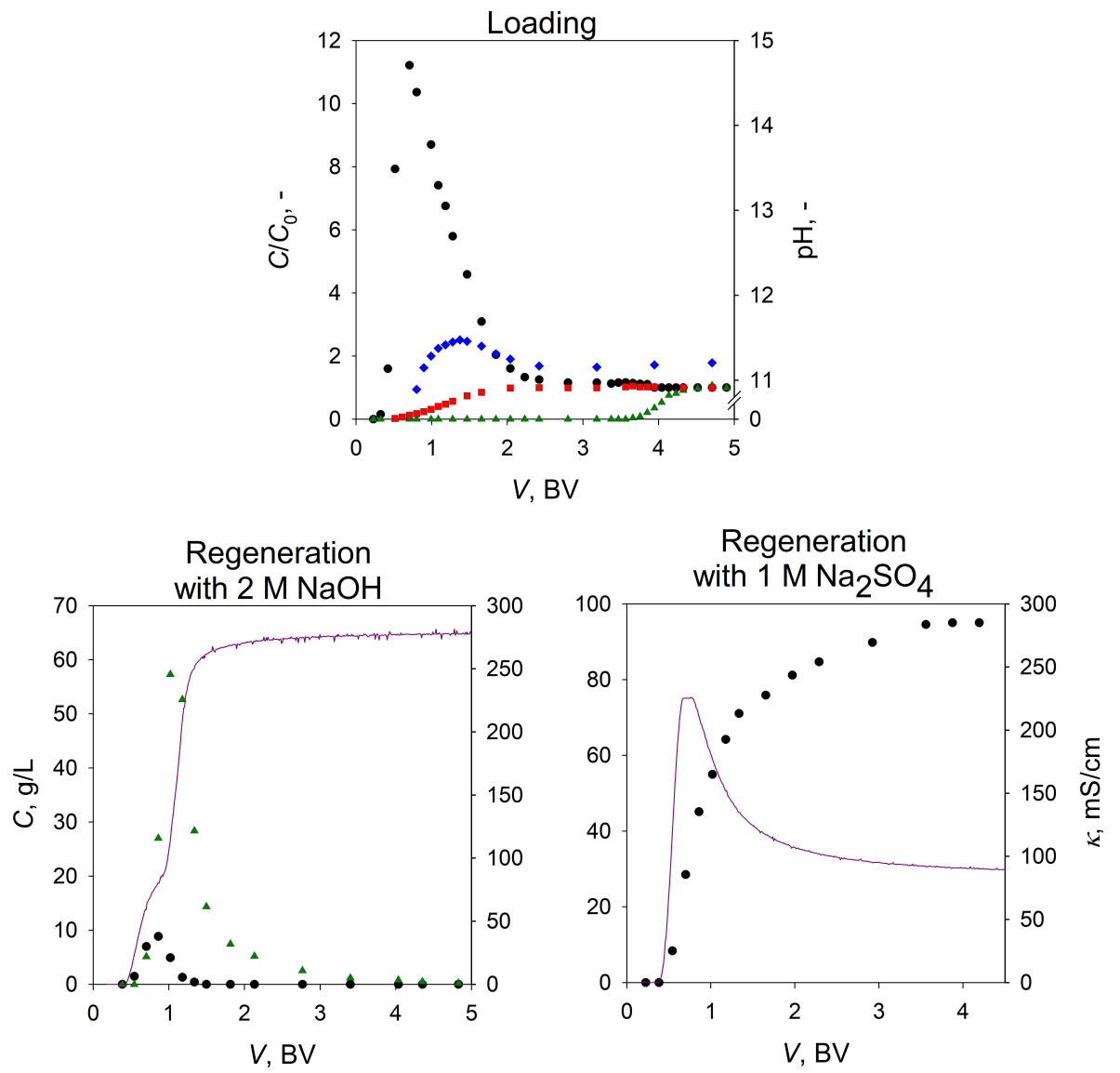


Figure 4

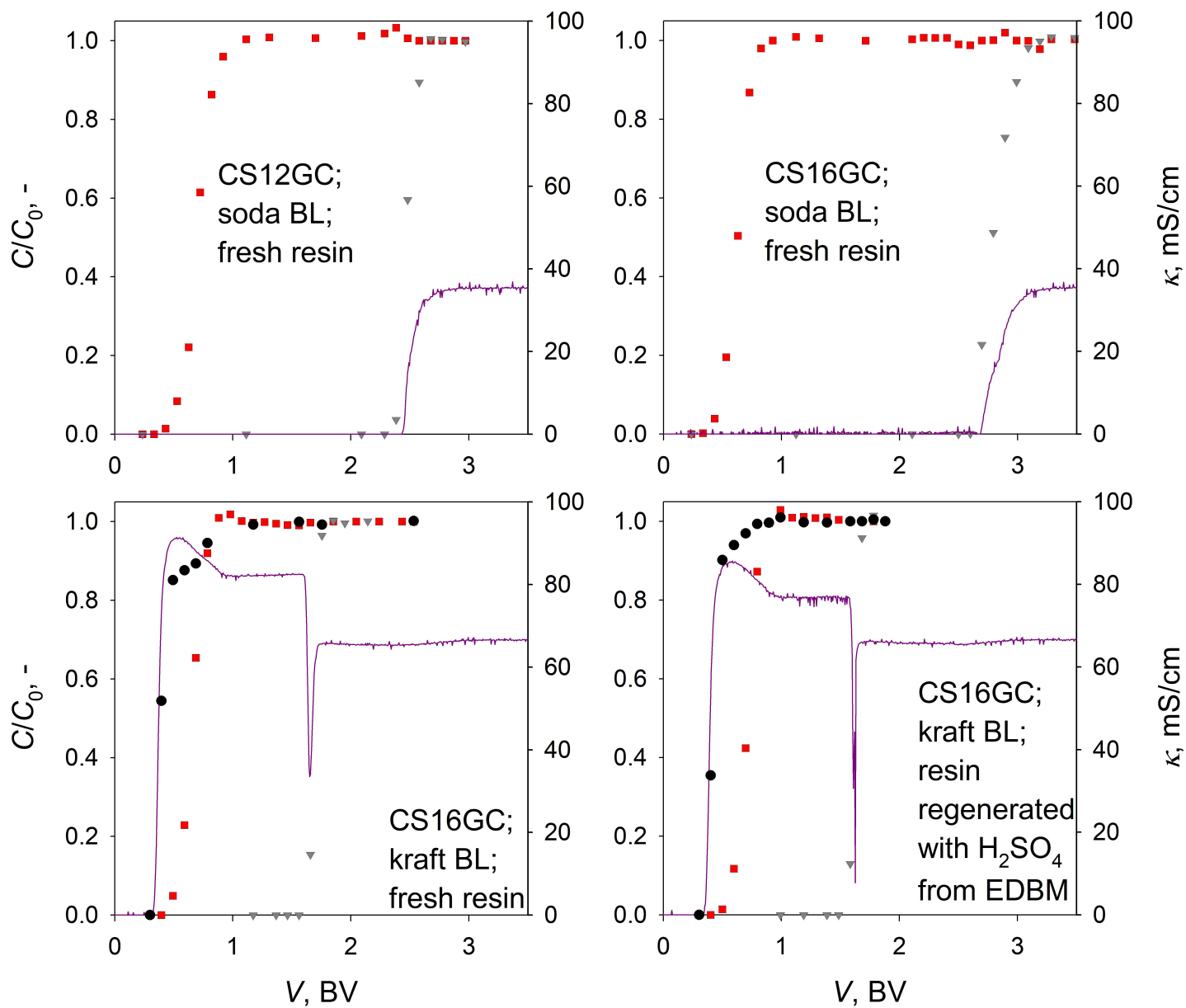


Figure 5

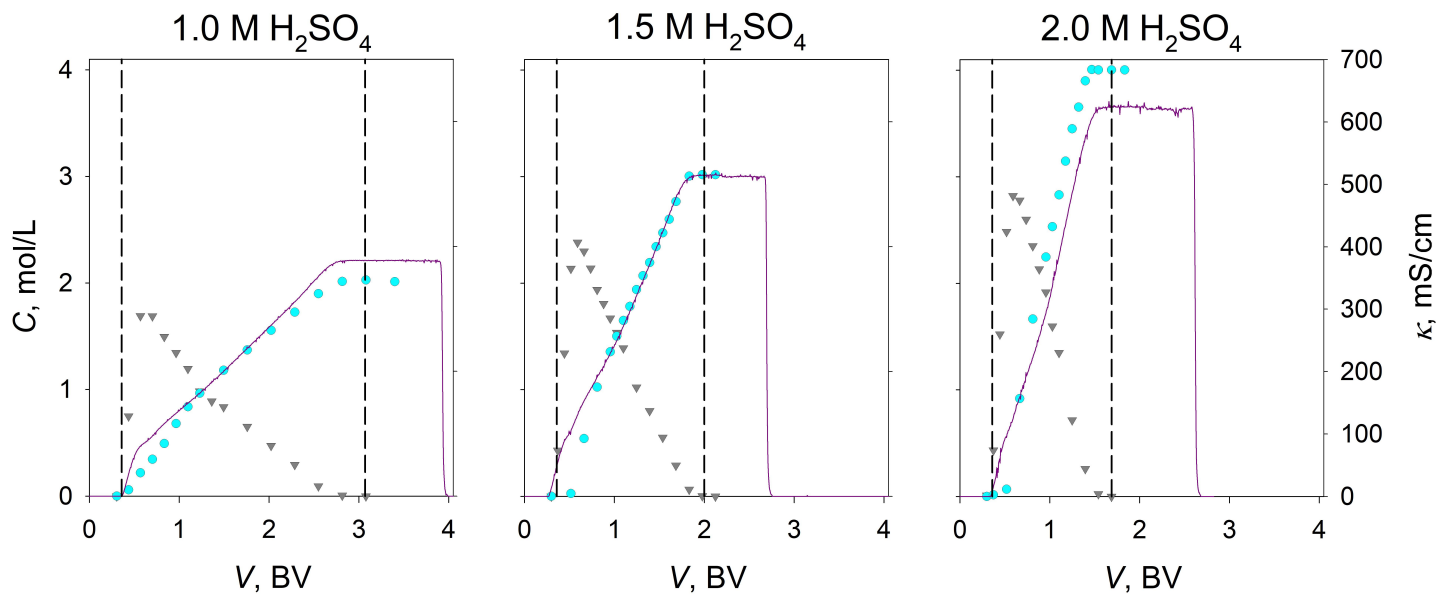


Figure 6

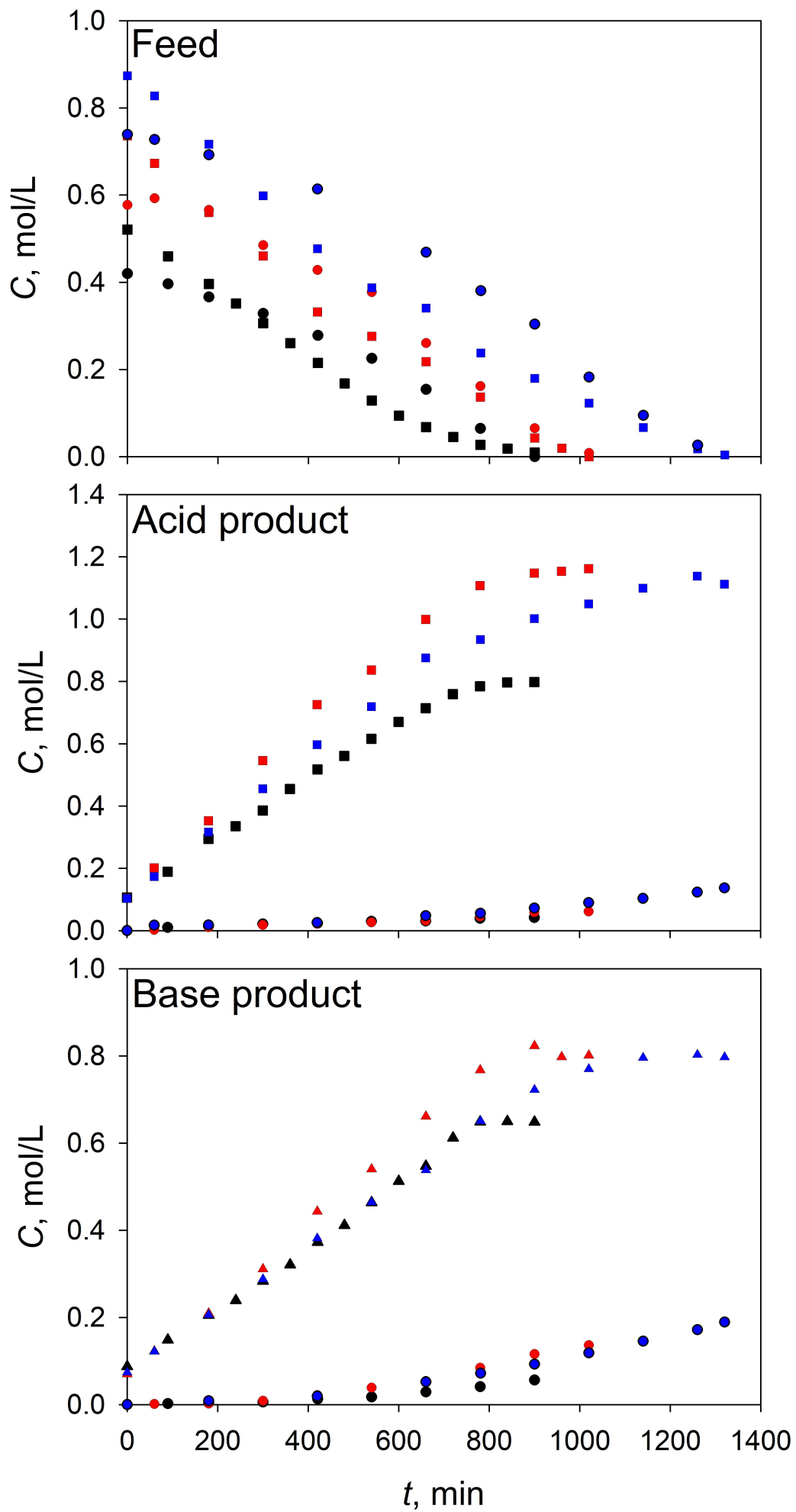


Figure 7

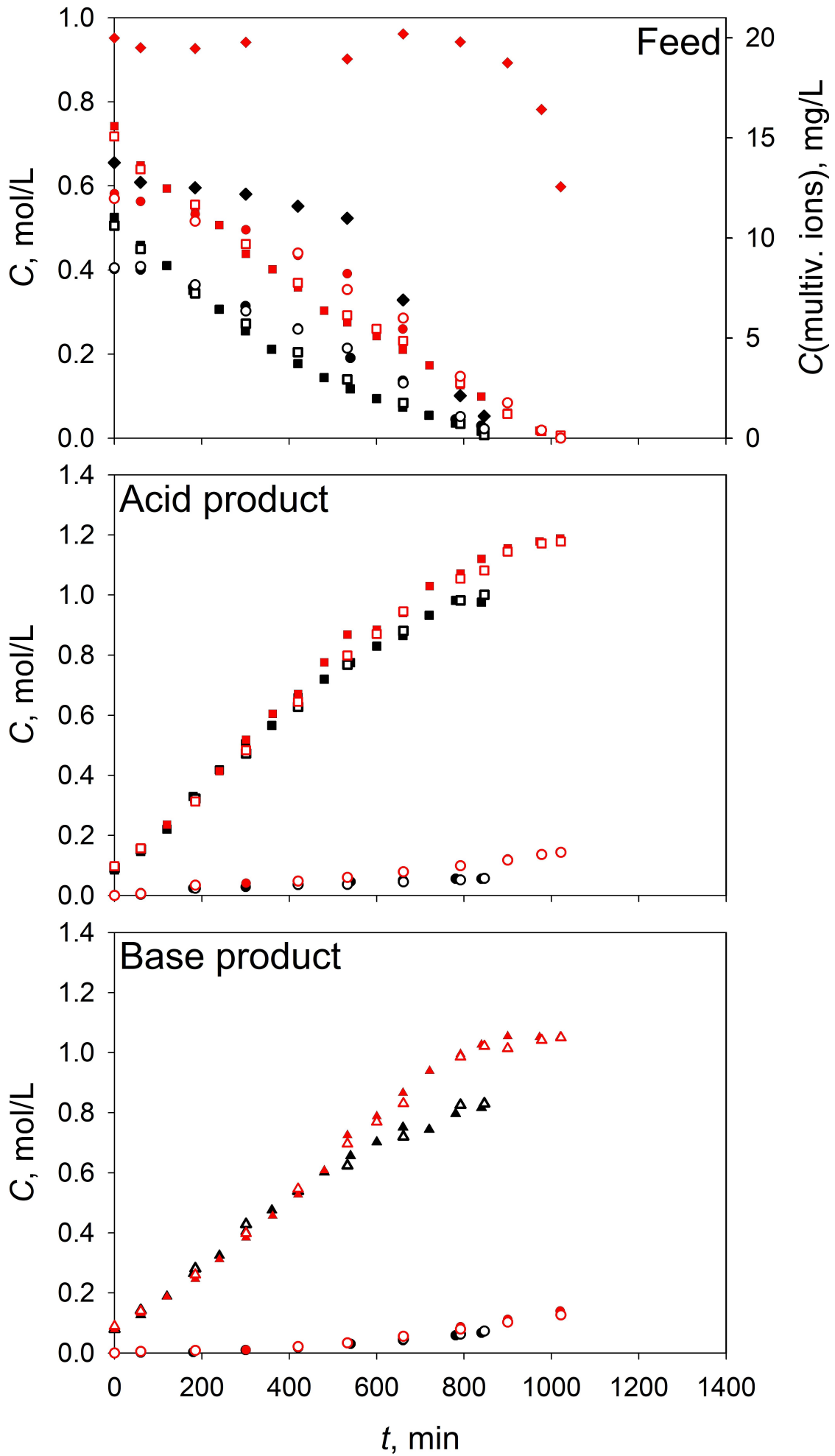
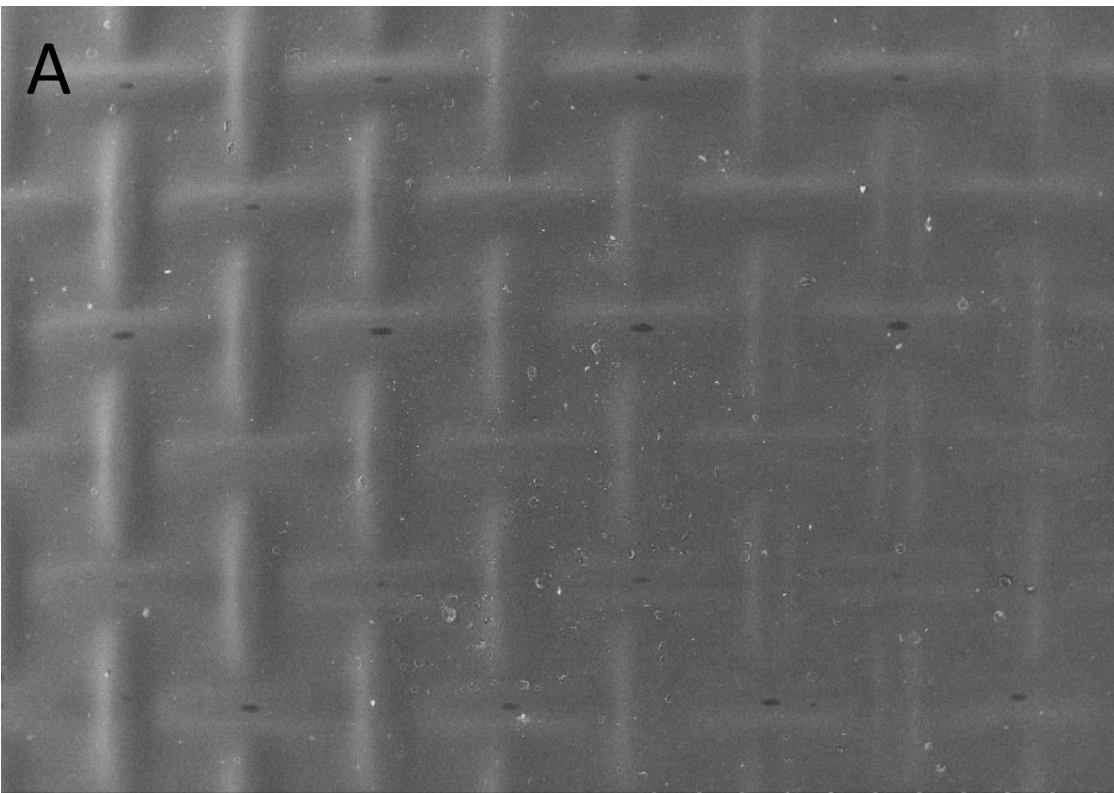


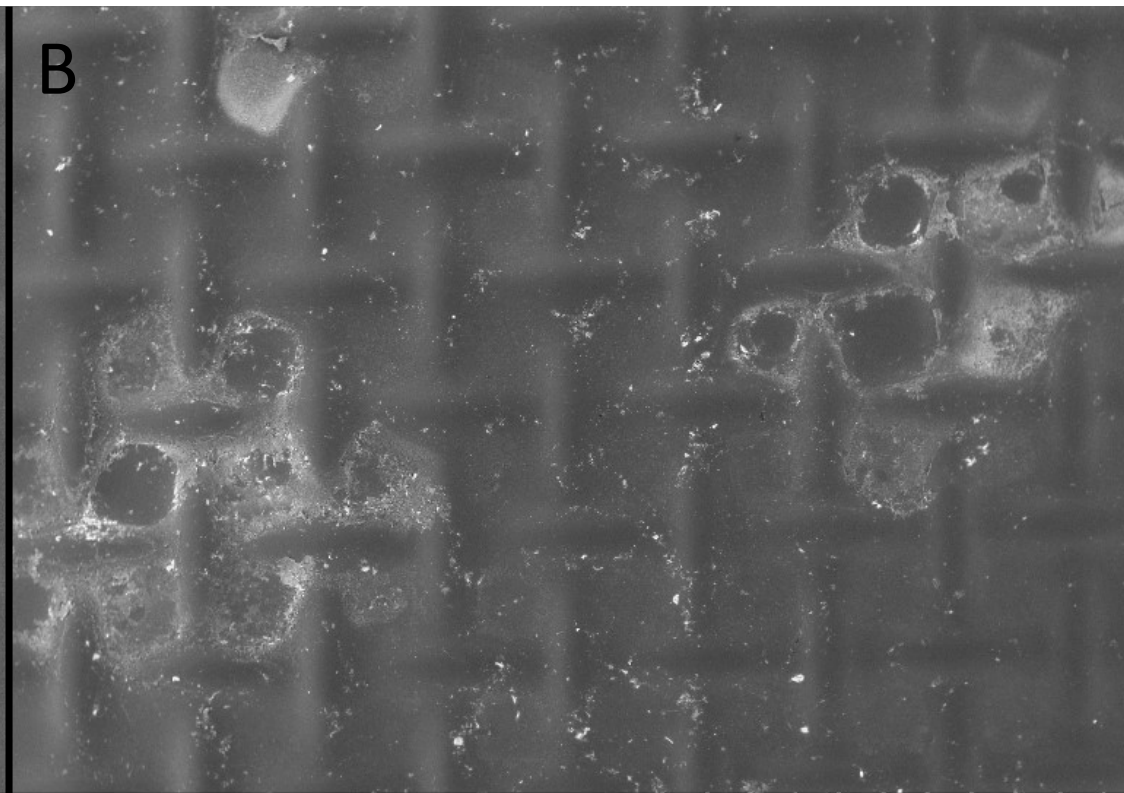
Figure 8





LUT 10.0kV X50 BSE-3D 50Pa

1.00mm



LUT 10.0kV X50 BSE-3D 50Pa

1.00mm

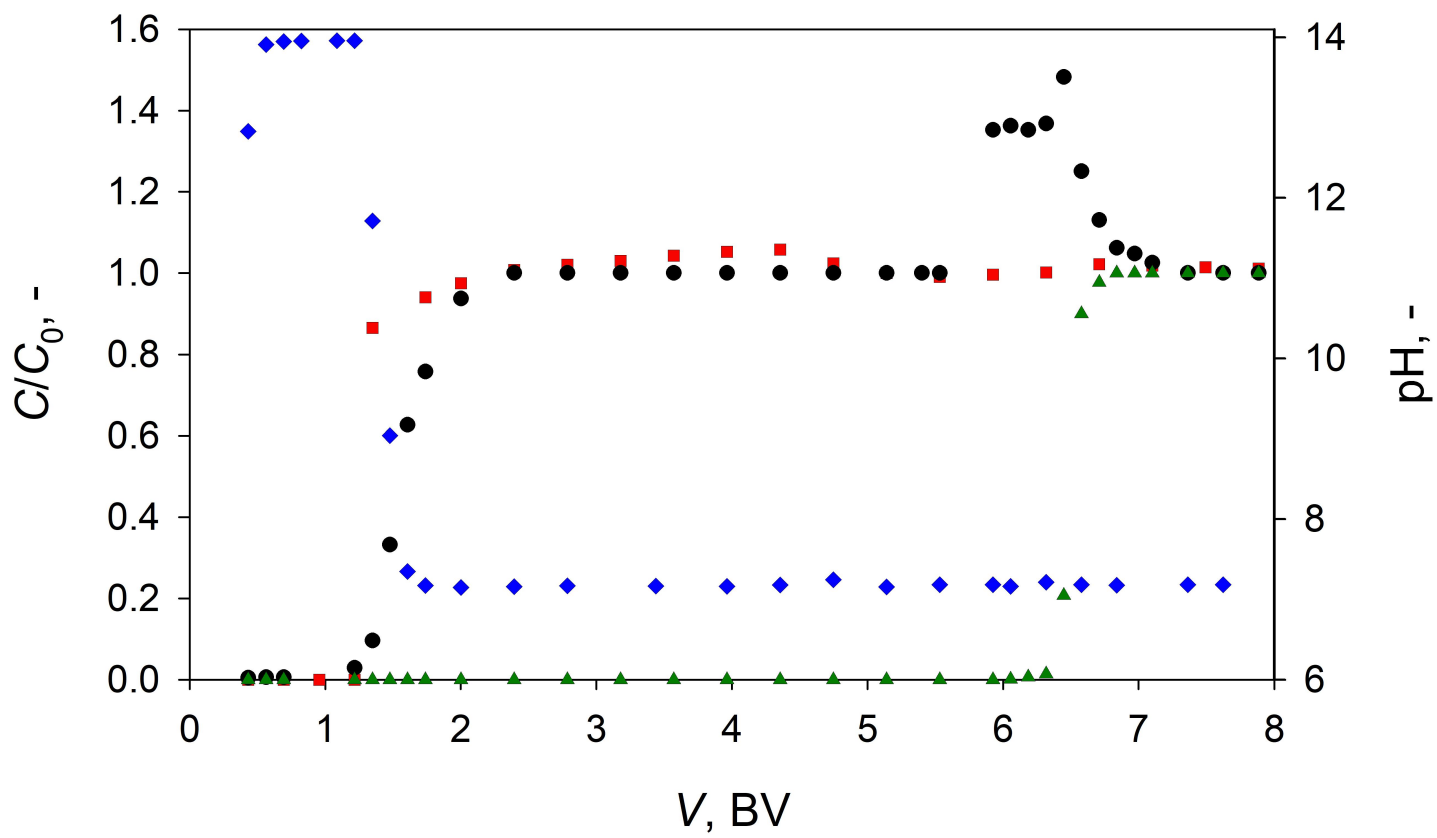


Figure S1

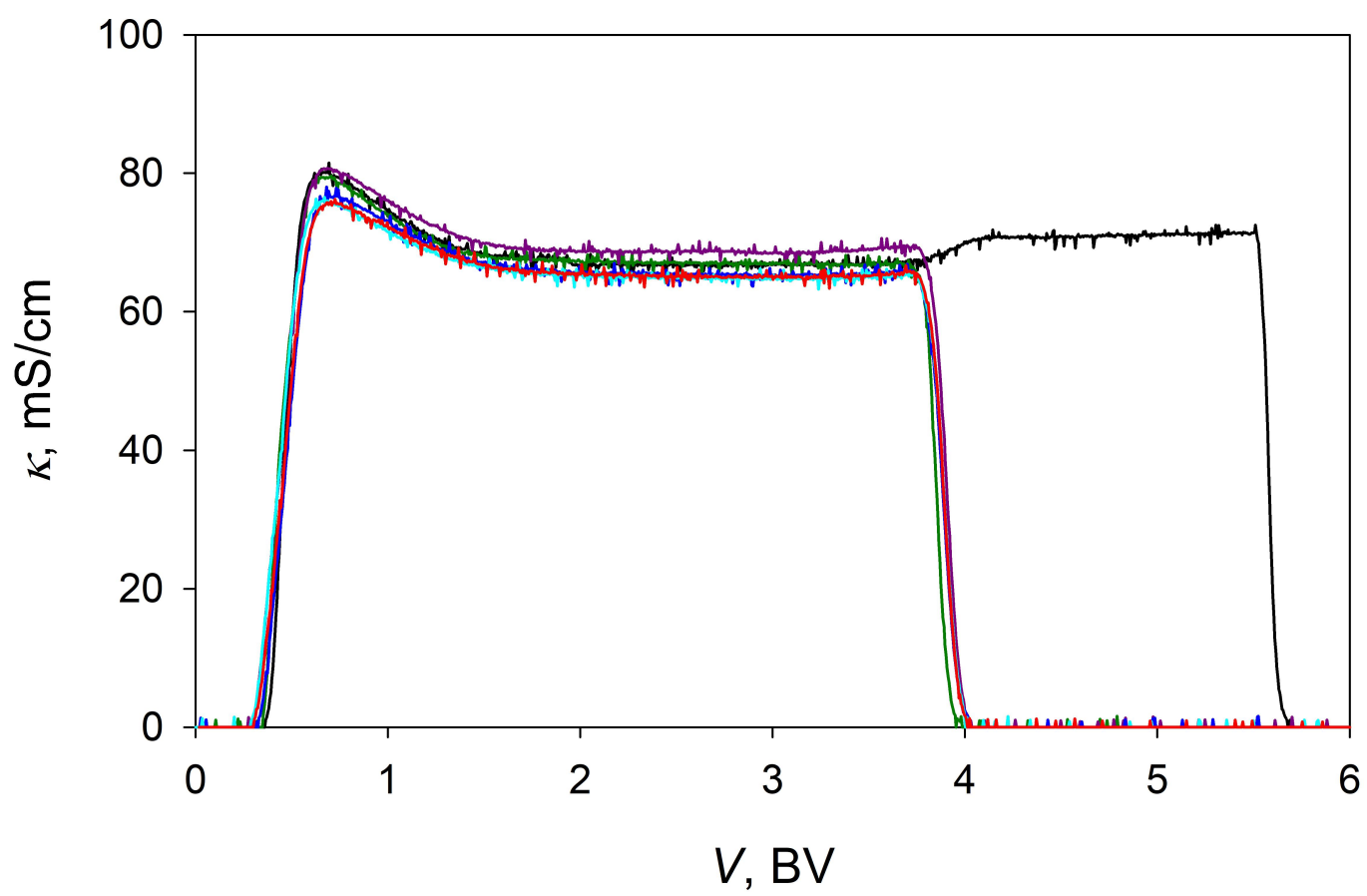


Figure S2

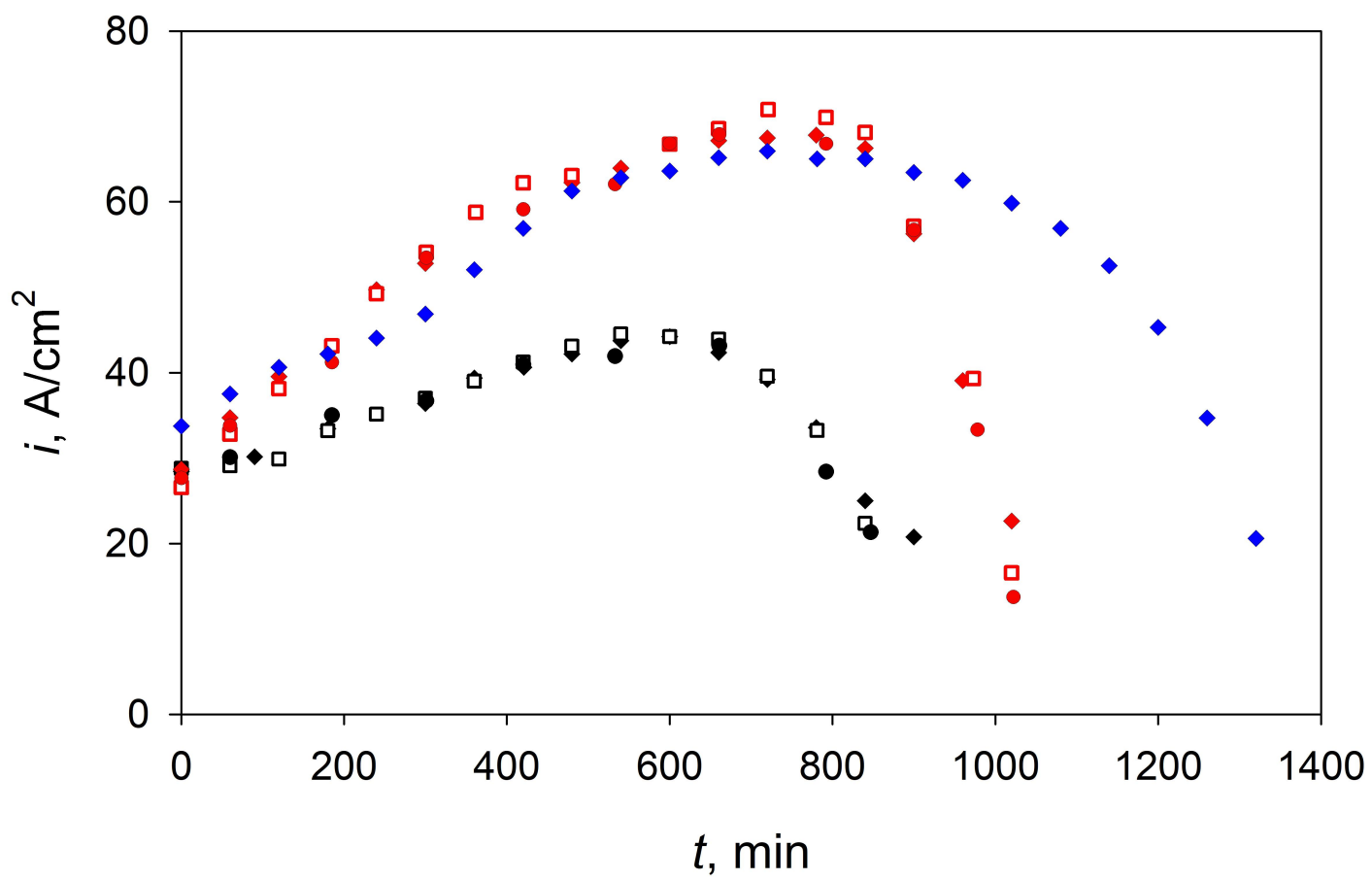


Figure S3

Table 1. Composition of the alkaline mixtures of Na<sup>+</sup> salts of HAs used as feed solutions in the ion exchange steps.

Compound	Concentration, g/L	
	Soda BL	Kraft BL
Na <sup>+</sup>	17.85	31.71
SO <sub>4</sub> <sup>2-</sup> *	0.00	6.87
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.00	11.84
Lignin	0.52	0.74
HAs	42.13	47.33
GA	2.08	3.83
FA	3.82	15.07
GISAs	12.33	9.46
XISA	4.09	1.05
LA	6.08	4.33
AA	5.99	8.75
2,5-DHPA	2.10	2.25
2-HBA	5.65	2.59

\* Due to alkaline pH, no molecular H<sub>2</sub>SO<sub>4</sub> or HSO<sub>4</sub><sup>-</sup> was present.

\*\* Quantified in H<sup>+</sup> form.

Table 2. Ion exchange resin characteristics. Abbreviations: SAC = strong cation exchange resin; SBA = strong anion exchange resin.

Separation material	Manufacturer	Type	Matrix	Functional group	Water content, % <sup>#</sup>	$Q_v$ , meq/mL <sup>#</sup>	$d_p$ , $\mu\text{m}$ <sup>#</sup>
CS12GC	Finex/Johnson–Matthey	SAC	PS-DVB	Sulfonic acid	59.3 (H <sup>+</sup> )	1.62 (H <sup>+</sup> )	220 (H <sup>+</sup> )
CS16GC	Finex/Johnson–Matthey	SAC	PS-DVB	Sulfonic acid	52.2 (H <sup>+</sup> )	1.93 (H <sup>+</sup> )	220 (H <sup>+</sup> )
IRA-958	Dow	SBA, type 1*	Acrylic-DVB	Quaternary amine	66–72 (Cl <sup>-</sup> )	0.80 (Cl <sup>-</sup> )	630–850 (Cl <sup>-</sup> )
Dowex 1X8	Dow	SBA, type 1*	PS-DVB	Quaternary amine	39–45 (Cl <sup>-</sup> )	1.20 (Cl <sup>-</sup> )	149–297 (Cl <sup>-</sup> )
AA16GC	Finex/Johnson–Matthey	SBA, type 1*	Acrylic-DVB	Quaternary amine	45.0 (Cl <sup>-</sup> )	1.38 (Cl <sup>-</sup> )	395 (Cl <sup>-</sup> )
AS542GC	Finex/Johnson–Matthey	SBA, type 2**	PS-DVB	Quaternary amine	45.0 (Cl <sup>-</sup> )	1.30 (Cl <sup>-</sup> )	375 (Cl <sup>-</sup> )

\* The functional group is trimethylammonium.

\*\* The functional group is dimethylethanolammonium.

# Measured in the ionic form given in the parentheses. Information provided by the manufacturer.

Table 3. Membrane characteristics.

Membrane	Type	Thickness, mm	$Q_w$ , meq/g	Stability C/pH	Water splitting efficiency/selectivity, %
FKB-PK-130	Cation exch.	0.126–0.14	0.9 (Na <sup>+</sup> )	$C(\text{KOH}) \leq 4$ mol/L (25 °C)	98 <sup>s</sup>
FAB-PK-130	Anion exch.	0.115–0.138	0.8 (Cl <sup>-</sup> )	pH = 1–14	> 95 <sup>s</sup>
FBM	Bipolar	0.13–0.16	-	pH = 1–14	> 98 <sup>w</sup>

<sup>s</sup> Selectivity 0.1/0.5 mol/L KCl at 25 °C.

<sup>w</sup> Water splitting efficiency at 100 mA/cm<sup>2</sup> current density in 0.5 mol/L NaCl (25 °C).

Table 4. Compositions of the feed solutions for EDBM.

Feed solution identifier	A	B	C
$C(\text{H}_2\text{SO}_4)_{\text{target}}$ , mol/L	1.0	1.5	2
$C(\text{Na}_2\text{SO}_4)_{\text{feed,initial}}$ , mol/L *	0.39	0.56	0.71
$C(\text{H}_2\text{SO}_4)_{\text{feed,initial}}$ , mol/L **	0.55	0.77	0.95
$C(\text{Na}_2\text{SO}_4)/C(\text{H}_2\text{SO}_4)$ , mol/mol	0.72	0.73	0.74
$C(\text{lignin})$ , g/L	0	0	0
$C(\text{M})_{\text{feed,initial}}$ , mg/L	13.76	19.99	n.a.
Mg	0.45	0.66	n.a.
Al	0.3	0.44	n.a.
Cr	1.39	2.02	n.a.
Fe	7.17	10.01	n.a.
Ni	0.46	0.73	n.a.
Cu	1.72	3.29	n.a.
Ca	2.27	2.84	n.a.

\* Based on  $\text{Na}^+$  concentration obtained by atomic absorption spectrometer.

\*\* Based on titration results for  $\text{H}^+$ .



Table 5. The efficiency of  $\text{S}_2\text{O}_3^{2-}$  removal from the kraft-BL-based feed with SBA resins in  $\text{OH}^-$  form.  $m_{\text{in}}$  = amount of  $\text{S}_2\text{O}_3^{2-}$  taken up by the resin;  $m_{\text{out}}$  = amount of  $\text{S}_2\text{O}_3^{2-}$  eluted with 3 BV of 2 mol/L NaOH.

Resin	$m_{\text{in}}$ , g	$m_{\text{out}}$ , g	$Y(\text{S}_2\text{O}_3^{2-})$ , %
1X8	0.88	0.22	25.0
AA16GC	0.86	0.3	34.9
AS542GC	1.35	1.34	99.3
IRA-958	0.25	0.28	112.0