Recovery of Sulfuric Acid from Fermentation Wastewater by Bipolar Electrodialysis – Effect of different Pretreatment Technologies Appendix

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APPENDIX A

It can be assumed that limiting current density (LCD) is governed by the transport of monovalent ions due to their larger transport numbers compared to divalent ions [1]. Thus, four NaCl solutions with decreasing concentration (12.4–0.6 g/L) were prepared to determine the ED stack's LCD with AEM and mCEM. The first NaCl solution matched the conductivity of the treated fermentation effluent, whereas the other three imitated decreasing diluate concentration during the ED demineralization. According to the Cowan and Brown [2] plots, an LCD was found for each NaCl solution and plotted against the solution's conductivity (Figure A1). The obtained correlation was linear, and LCD values were multiplied by a safety factor 0.8 to establish operating current density for the ED experiments with fermentation effluent. These four values were applied step-wise, from highest to lowest, until the diluate conductivity decreased to ~1 mS/cm.
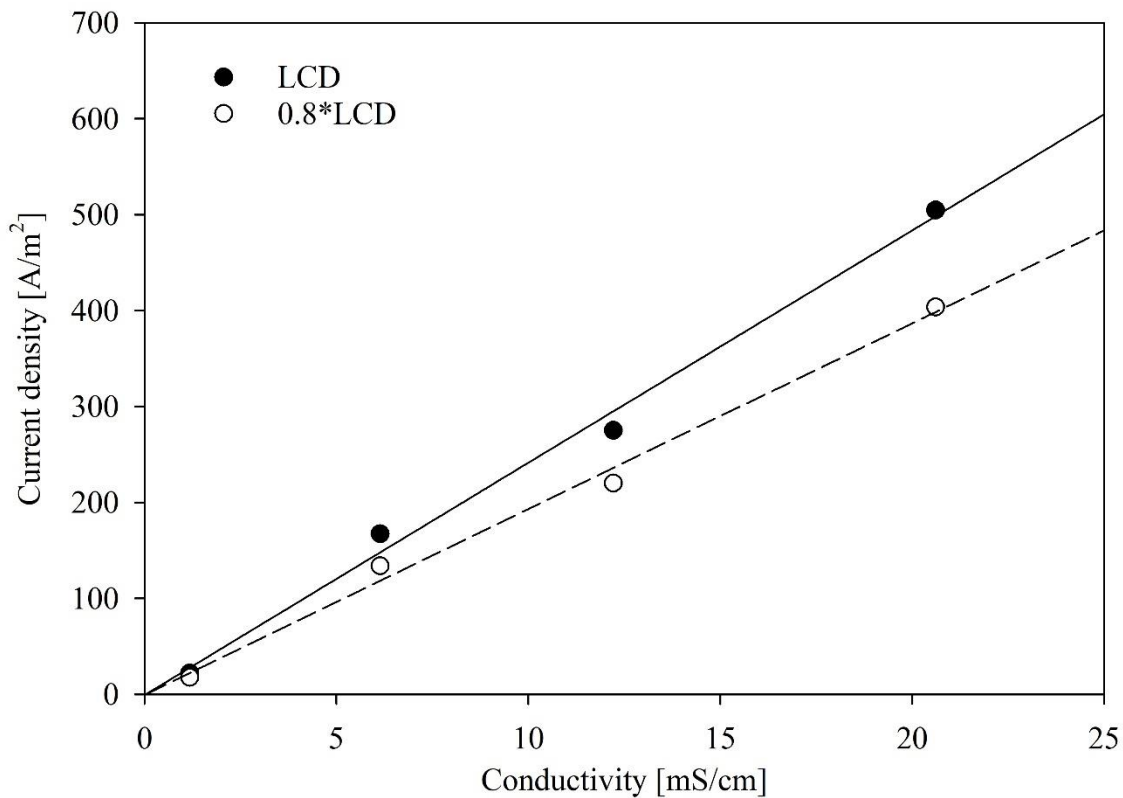

Figure A1. Limiting current density and operating current density (0.8LCD) plotted against the feed conductivity.

APPENDIX B

Perm-selectivities were determined for three sampling points during the ED process, at average current densities of 209.4 A/m^2, 143.8 A/m^2 and 78.1 A/m^2, for both first and the second ED run (Figure B1), The sampling points were accordingly at process time 21 min, 54 min and 137 min for the first ED run (Figure B1a), and 19 min, 51 min and 144 min for the second ED run (Figure B1b). Perm-selectivity of Na$^+$, NH-4 and K$^+$ against Mg^{2+} was in general higher than for the same monovalent cations against Ca^{2+}. This trend can be assigned to the lager Stokes radius (3.47>3.10 Å) and smaller self-diffusion coefficient (0.705*10^{-9}<0.793*10^{-9} m^2/s) of Mg^{2+} than for Ca^{2+} ions [3]. With decreasing diluate ion concentration and current density, the perm-selectivities were increasing, indicating a positive effect of these two parameters on the overall membrane selectivity. However, in the second ED run the perm-selectivities decreased drastically, up to 67% for e.g. Na$^+$/Mg^{2+} ratio after first 20 min of the ED process when first and the second ED run were compared. With prolonged ED operation time the discrepancy between the membrane selectivity of two ED runs became even more pronounced. When the fluxes of divalent cations through the mCEM of the first and the second ED run were compared, a significant increase could be observed (Figure 4b). The initially higher fluxes (first 20 min) are assigned to the very low ionic strength in the concentrating compared to diluting chamber, as it can be seen from Figure 6 and Figure 2. These values drop by 50% for Ca^{2+} and 40% for Mg^{2+} with the increasing concentrate concentration. Further on, an above 2 times increased Mg^{2+} and Ca^{2+} flux in the second ED run was recorded (Figure 4b), as explained in Section 3.5 of the main document.
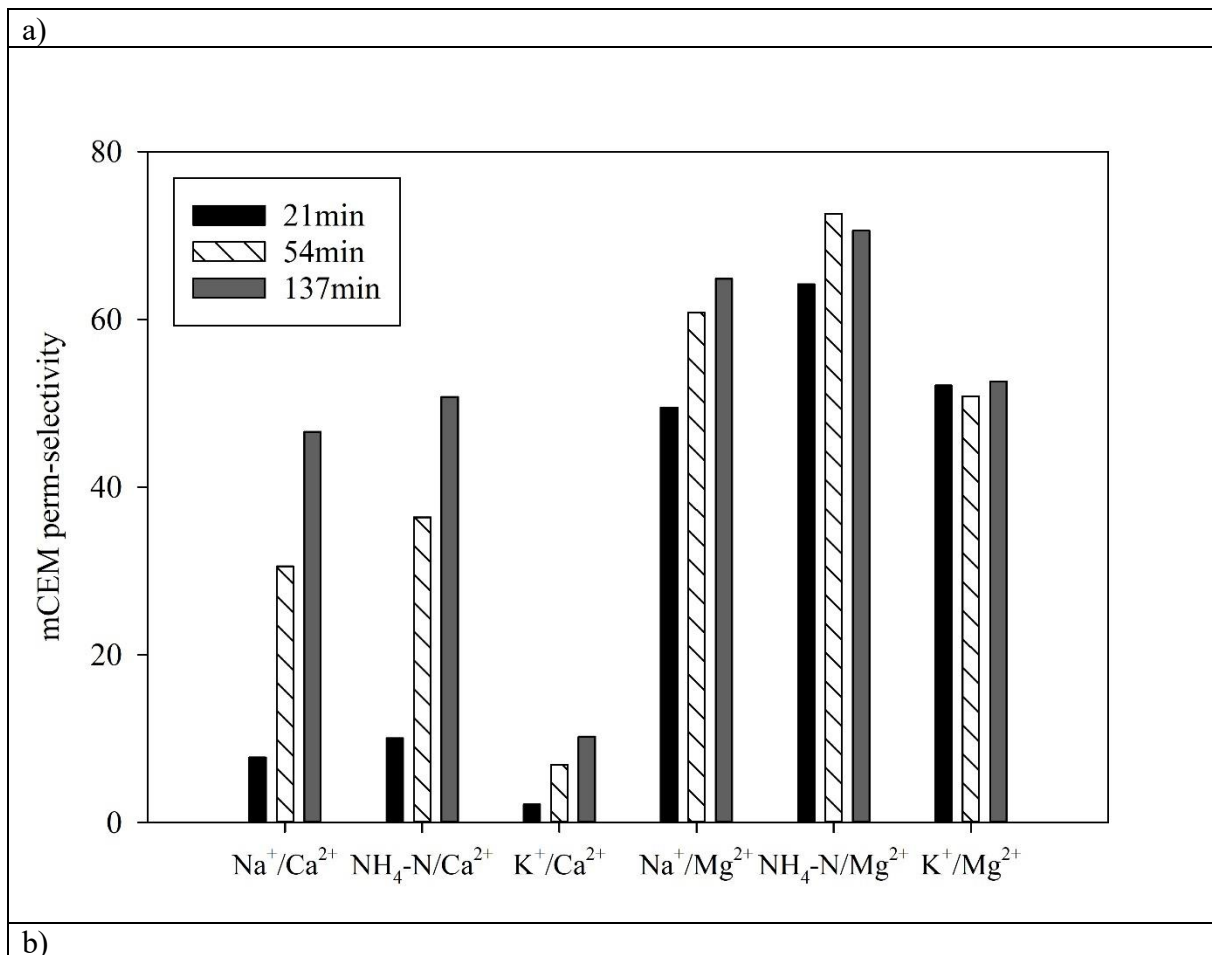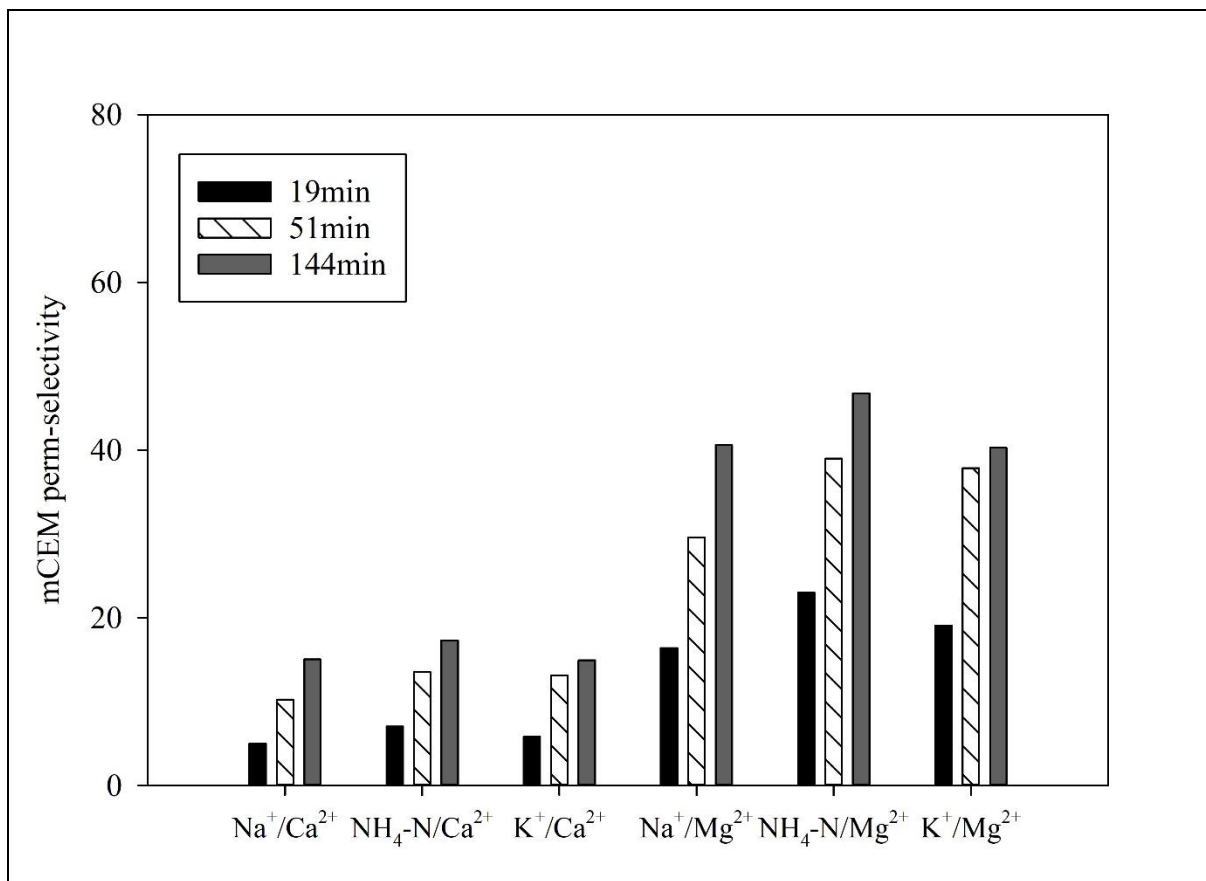
Figure B1. Perm-selectivity between mono-a nd divalent cations through mCEM in ED runs; a) in the first ED run, and b) in the second ED run.

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