A robust batch RO technology to overcome the barriers to full circularity in Cr(III) electroplating operations

Roxanne Engstler[a,b], Ebrahim Hosseinipour[c], Seval Yilmaz[c], Felix Heinzler[d], Marvin Wagner[d], Mathias Ulbricht[b], Philip Davies[c], Stéphan Barbe[a,e,*]

[a] Faculty of Applied Natural Sciences, Technische Hochschule Köln, 51379 Leverkusen, Germany

[b] Department of Technical Chemistry II, University of Duisburg-Essen, 45141 Essen, Germany

[c] School of Engineering, University of Birmingham, B15 2FG Birmingham, UK

[d] BIA Kunststoff- und Galvanotechnik GmbH & Co. KG, 42655 Solingen, Germany

[e] The Institute of Advanced Studies, University of Birmingham, B15 2TT Birmingham, UK

*stephan.barbe@th-koeln.de

WORKING PRINCIPLE OF THE HYBRID RO

The operation of a hybrid RO system can be divided in three phases, depending on the valves states. In the semi-batch pressurization phase (Figure S1, (a)) wastewater is continuously fed through the membrane module and work exchanger via the high-pressure pump and recirculation pump.

Purified water leaves the system as permeate whereas concentrate is retained due to the closed concentrate valve. Proper mixing is achieved by means of a recirculation pump. During this phase, the osmotic pressure increases linearly with the concentration of plating chemicals, whereas water recovery only increases asymptotically.[1]

At the switch point, the bypass valve closes and the batch pressurization phase begins (Figure S1, (b)). The recirculation pump ensures proper mixing of the concentrate through the system, whereas the high-pressure pump moves the piston of the work exchanger, continuously reducing the volume of the retentate. Now water recovery increases linearly, whereas the concentration increases with increasing rate. When the piston reaches the end of the pressure vessel, the recirculation valve closes and the concentrate valve opens, releasing the concentrate from the plant (Figure S1, (c)). Simultaneously, the bypass valve opens so fresh feed is introduced to the system, pushing the piston to the start position and purging the concentrate out of the system. For more detailed information on the working principle,[2] or theoretical background,[1] please refer to published literature.

The permeate flux of the semi-batch and batch phase can be chosen independently from each other. In standard operation a flux of 10 LMH in semi-batch and 5.7 LMH in batch mode proofed to be a viable option for an operation achieving high water recovery in a reasonable time scale.
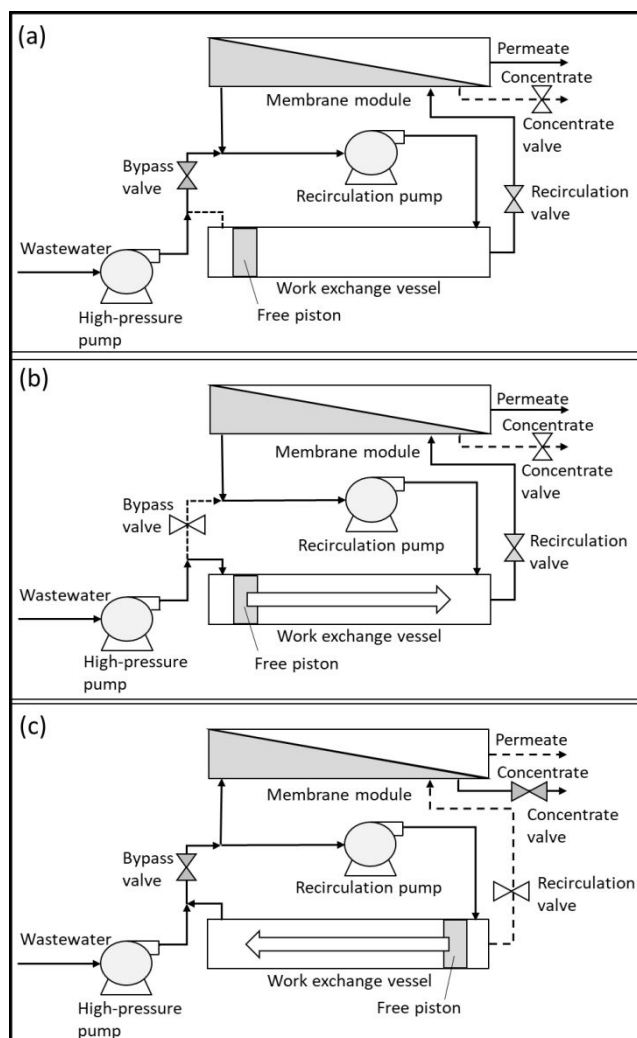

Figure S1. Working principle of the hybrid semi-batch/batch RO process divided in three phases: (a) semi-batch RO, (b) batch RO and (c) purge-and-refill phase. Recreated with permission from Karimi et al.[3]

EXPERIMENTAL

Evaluation of Membrane Feasibility for 2nd Gen Electrolyte Using Lab-Scale Reverse Osmosis Experiments. For the lab scale evaluation, a bench-top RO rig (see Figure S2) was temporarily setup in the electroplating facility of BIA

(Solingen, Germany), kindly provided by CUT Membrane Technology (Erkrath, Germany).

Figure S2. Photograph of the bench-top RO lab plant used in this work.

The experiments were conducted using a 80 cm² flat sheet of high-pressure membrane XUS180808 (DuPont™; DuPont de Nemours (Deutschland) GmbH, Deutschland) under constant permeate flux of 10 LMH. The flow velocity above the membrane was set to 0.6 m/s and 2.1 m/s (Reynold number of 981 and 3269), using a bypass valve (dashed line, Figure S3).
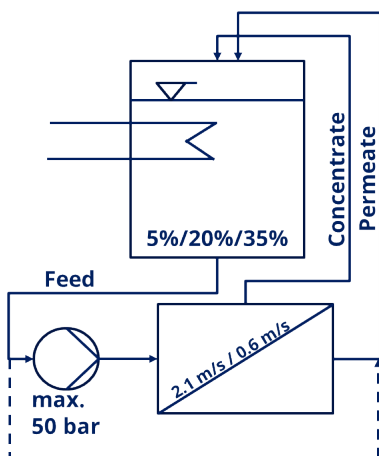

Figure S3. Piping and instrumentation scheme of RO lab plant with experimental conditions.

Commercial Plating Electrolyte solutions. The information on concentration range and optimum values of sulfate, chromium and boric acid of the 1st and 2nd gen electrolyte (cf. Table 1) is provided by the manufacturer (MacDermid Enthone),[4,5] TOC values were measured and osmotic pressure was estimated using water activity measurements, both described in this section.

Electrical conductivity. The electrical conductivity of rinse water samples was determined with a hand-held GLF100 device (Geisinger electronic GmbH, Germany).

ICP-OES. Spectroscopic determination of chromium, sulfur and boron was carried out by means of inductively coupled plasma optical emission spectrometry (ICP-OES, SPECTROGREEN, SPECTRO Analytical Instruments GmbH, Germany) for RO feed, concentrate, permeate and rinse water

samples. The contents of sulfate and boric acid were derived from these data. Permeates were measured directly, whereas concentrates, feed solutions and rinse water were determined in dilution (1:100, 1:10, 1:10, respectively). Average values were calculated from triplicates..

Osmotic Pressure. The osmotic pressure (π in bar) of rinse water and of solutions from the stirring cell experiments were calculated using the following equation

$$\pi = 0.01\ n\text{wRT}$$

with the osmolality (n in Osmol/kg) values determined with the OSMOMAT 3000 freezing point osmometer (Gonotec®, Meß- und Regeltechnik GmbH, Germany), where the water density w was 1 kg/L. Average values were calculated from triplicates.

Total Organic Carbon. For all TOC analyses the TOC analyser multi N/C 2100 S (analytikjena, Germany) with software multiWin 4.09 was used. The samples were automatically acidified with phosphoric acid (10%) and combusted in an oxygen stream at 800°C. TOC was determined automatically using the difference method (TOC = TC-TIC). The calibration used ten combined inorganic/organic carbon (IC/OC) standards, following the standardised procedure from DIN EN 1484. Potassium hydrogen phthalate was used as OC source and sodium carbonate and sodium hydrogen carbonate were used as IC sources.[6]

Evaluation of Membrane Feasibility for 2nd Gen Electrolyte Using Lab-Scale Reverse Osmosis Experiments. A bench-top RO rig (Photo see Supporting information (SI)) was temporarily setup in the electroplating facility of BIA (Solingen, Germany), kindly provided by CUT Membrane Technology (Erkrath, Germany). The maximum operating pressure was 50 bar with a feed volume of 2 L. Water-cooling provided experimental temperatures of 20-23°C. Steady-concentration experiments were carried out by re-mixing RO concentrate and permeate in the feed tank. The concentration increase of a RO batch operation was mimicked by using feeds of different concentrations. The experiments were conducted using a 80 cm² flat sheet of high-pressure membrane XUS180808 (DuPont™; DuPont de Nemours (Deutschland) GmbH, Deutschland) under constant permeate flux of 10 LMH. The flow velocity above the membrane was set to 0.6 m/s and 2.1 m/s (Reynold number of 981 and 3269), using a bypass valve (see scheme in SI, indicated with dashed line).

Membrane permeance and salt rejection were measured after the 1st, 3rd and 6th experiment, using deionized (DI) water (<10 µS/cm) and a sodium chloride solution (20 g/L Acros Organics, 99%).

Artificial rinse water was prepared as feed by dilution of a 2nd gen electrolyte with DI water (1:20/1:5/1:2.85) corresponding to 5%/20%/35% respective electrolyte concentration. The 2nd gen electrolyte originated from the plating bath at BIA Solingen (Germany). This preparation procedure ensured a realistic representation of rinse water with increasing recovery. The osmotic pressure π of the feeds were derived from water activity a_w measured with the vapor pressure osmometer AQUALAB® 4TEV (METER Group, Inc., Pullman, WA, USA) using the non-simplified van't Hoff equation:

$$\pi = -\left(\frac{RT}{V_m}\right)\ln(a_w)$$

with the molar gas constant R, temperature T and molar volume of water V_m. Please note that the osmotic pressures of diluted electrolyte samples were used for the investigation of possible monitoring strategies (see Monitoring Strategies section).

The concentrations of chromium and boric acid in the feeds were determined by means of ICP-OES and are listed in Table S1:

Table S1. Average mass concentration of chromium and boric acid in the RO feeds.

$c_{Feed}/c_{Electrolyte}$ / vol%		5%	20%	35%
Feed	Chromium / mg/L	359	1441	2312
	Boric acid / g/L	4.6	18.2	30.1

Robustness Test of the Hybrid RO Treatment. The pilot scale hybrid RO rig, located at the University of Birmingham, was used. These experiments were conducted with a maximum pressure of 110 bar. The switch point was chosen by the peak pressure method.[3] The membrane specifications are listed in Table S2. Following specifications were selected for the Design of Experiment (DOE) using the Minitab software (Minitab® 21.4.2):

Factors: 4 (feed dilution, feed temperature, recirculation pump flow, permeate flux) **Resolution**: IV, **Runs**: 11, **Replicates**: 1, **Fraction**: ½, **Blocks** 1, **Centre points (total):** 3. The variance of experiments was derived from the variance of the center point.

Table S2 Specifications of the membrane module.[7]

Membrane	DuPont™ XUS180808
Element specification	8 inch spiral-wound module
Membrane type	Polyamide thin-film composite
Membrane area	30.6 m²
Feed spacer	34 mil (0.8636 mm)
NaCl rejection	99.7 % (min. 99.5%)
under standard test conditions	at 32,000 ppm NaCl, 55 bar, 25°C, pH 8, 8 % recovery
Maximum pressure	120 bar (for T ≤ 30°C)
Maximum operating temperature	45 °C
pH range	2-11 (1-13 short term cleaning)

According to the supplier's specifications, this membrane can be constantly operated at pressures up to 120 bar at 20-30°C.[7]

The recovery r of RO experiments at pilot scale was calculated with the following formula:

$$r = \frac{V_p}{V_f}$$

with the permeate volume V_p and the feed volume V_f determined by weight divided by the solution density. The density of 1 kg/L was used, because of the dilute nature of the feed and permeate.

The concentration factor was calculated with the following formula

$$CF = \frac{1}{1-r}$$

which resembles the concentration increase for components with rejections close to 100%.

The electrical SEC was calculated as the sum of the energy consumption of the high-pressure supply pump and recirculation pump, divided by the feed volume over a whole cycle:

$$SEC = \frac{E_{sp} + E_{rp}}{V_f}$$

Investigations on a 2nd Pass RO Treatment. Feed solutions containing 1/3.2/6.4/10 g/L boric acid (Sigma-Aldrich, ACS reagent, ≥99.5%) were prepared. The first representing a first stage RO permeate and the others representing the same permeate at 69%/84%/90% water recovery. Identical feed solutions were prepared with additional sodium sulfate (Fisher Scientific, anhydrous, 99%), resulting in molar ratios of 1:0/1:0.82/1:1.5 $B(OH)_3$ to SO_4^{2-}. The stirred (700 rpm) membrane cell (Sterlitech HP4750, max. 69 bar) was filled with 300 mL of feed solution. At a flux of 35.0 ± 0.9 LMH, a total of 22.5 mL permeate was produced. For analytical purposes, the first 5 mL of permeate were discarded. Each experiment was conducted in duplicate. The osmotic pressure of the feeds, retentates and permeates were measured using the Osmomat™ 3000 Basic (Gonotec® Meß- und Regeltechnik GmbH, Germany). Boric acid concentration was determined by means of titration.

The rejection for boric acid was calculated as follows:

$$R = \left(\frac{c_{FR} - c_P}{c_{FR}}\right) * 100\%$$

with c_{FR} being the average boric acid concentration of feed and retentate and c_P the concentration in the permeate of the same experiment.

Titrimetric Determination of Boric Acid. Boric acid concentrations of feed, retentates and permeates from stirring cell experiments were determined as follows[8]: 2.5 mL (5 mL for permeates) of sample was titrated with 0.02 M NaOH solution (Fisher scientific, analytical reagent grade), after addition of 50 mL sorbitol solution (1:1 by weight) using 0.1% bromcresol purple indicator solution. Each sample was titrated in duplicate. A third titration was performed when use of standard solution differed >0.1 mL, translating to 0.049 g/L accuracy (0.025g/L for permeates).

Characterization of Feed Water at BIA. At the start of the research project, BIA was already testing Cr(III) based electrolytes of the 1st gen in their facility in Slovakia. The first analysis of rinse water samples from this site is shown in Figure S4.
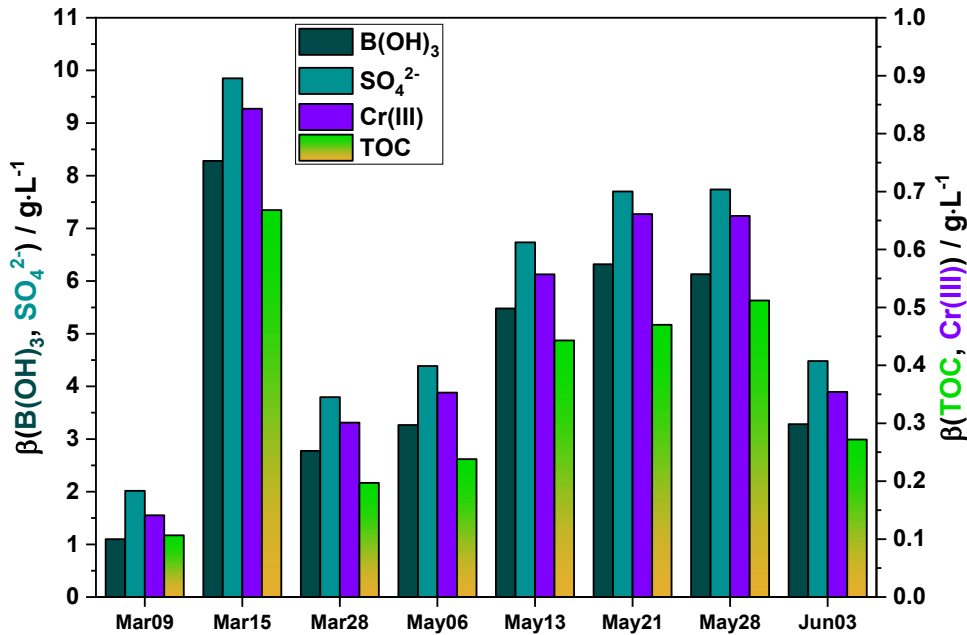

Figure S4. Mass concentration of boric acid, sulfate, chromium and TOC of rinse water samples of an industrial plating line using 1st gen Cr(III) electrolyte. Samples were taken right before rinse water tanks were drained and were kindly provided by BIA Plastic and Plating Technology Slovakia, s.r.o., (Slovakia).

Treatment of 1st Stage RO Permeate. Incorporating sulfate to the feed notably increases its osmotic pressure, detailed in
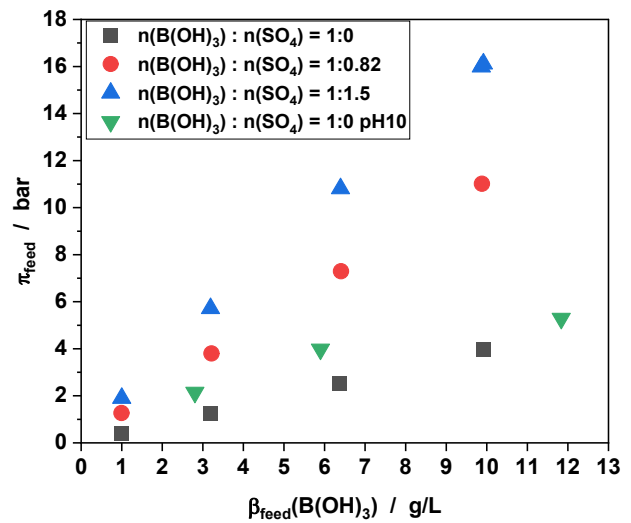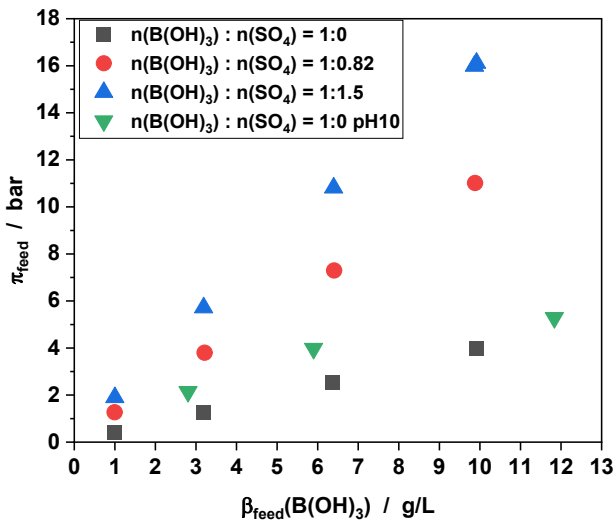

Figure S5.

Figure S5. Osmotic pressure of feeds with increased sulfate content: Without addition of sulfate (black squares), with addition of sulfate in the stoichiometric ratio found in rinses and 2nd gen electrolyte (1:0.82, red dots) and with a stoichiometric ratio of 1:1.5 (blue triangles). A feed at pH 10 (green triangles) is given for comparison.

Monitoring Strategies. The correlation between the concentrations of sulfate and boric acid is in shown in Figure S6.
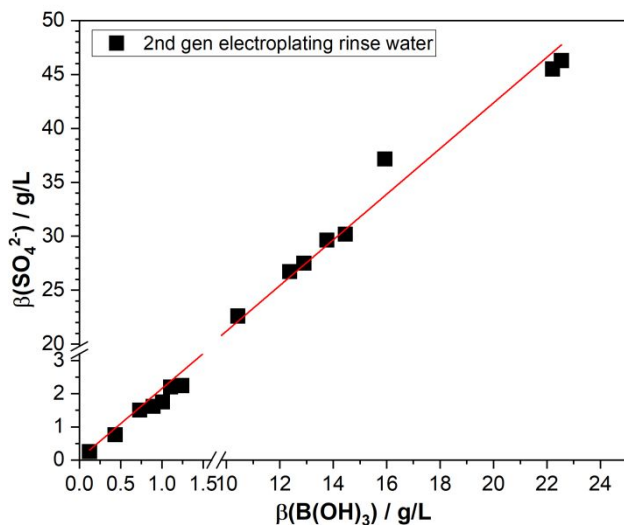
Figure S6. Mass concentration of sulfate and boric acid in electroplating rinse water. Cut axis to visually expand the area of low concentration.

Final RO Design. Major Unit Operations and sensors for the RO wastewater treatment plant are summarized in

Table **S3.**

Table S3. Major Unit Operations of the planned RO rig at BIA in Solingen (Germany).

Unit	Capacity	Sensor						Equipment	
		level	temperature	pressure	flow	conductivity	proximity	heater	top mixer
RO feed tank	2.5 m³	x	x			x		x	x
RO concentrate tank	0.5 m³	x	x					x	
RO permeate tank	2.5 m³	x	x		x				
CIP tank	0.6 m³	x	x						
RO feed pump	0.78 m³/h			x					
High-pressure RO pump	0.78 m³/h			x	x				
Recirculation pump	3.6 m³/h				x				
CIP pump	10 m³/h								
Work exchanging vessel	65 L			x			x		
Concentrate outlet				x		x			
Permeate outlet				x		x			

AUTHOR INFORMATION

Corresponding Author

* Stephan.barbe@th-koeln.de

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