

Separation of zinc and iron from secondary manganese sulfate leachate by solvent extraction

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ABSTRACT

Purification of concentrated manganese sulfate solution by solvent extraction is discussed in this paper. The use of bis(2-ethylhexyl) hydrogen phosphate (D2EHPA) and bis(2,4,4-trimethylpentyl)phosphinic acid (BTMPPA) was studied in removal of impurities from zinc electrowinning anode sludge leachates. Over 99 % of zinc and iron were removed by both extractants at around pH 3 in two mixer-settlers operating in continuous countercurrent mode at a solvent-to-feed (S/F) ratio of 0.43 and $T = 22 \pm 1$ °C. BTMPPA had higher selectivity for zinc and iron over manganese than D2EHPA under all experimental conditions. Extraction of manganese was typically below 10 % and can be limited by crowding the extractants, since the fraction of manganese in both loaded extractants was decreased by decreasing organic to aqueous volumetric ratio (O/A). A significant amount of the co-extracted Mn was recovered by selective stripping with 0.5 M sulfuric acid. Extraction by BTMPPA was more sensitive to pH adjustment than extraction by D2EHPA. Increasing the mean residence time in mixer from 3.6 min to 6.0 min improved the removal of zinc and iron with BTMPPA but the change in residence time had little or no effect on zinc and iron removal with D2EHPA.

1. Introduction

Manganese and zinc are widely used elements in the metallurgical industry. Most of the Mn is used in steelmaking (Matricardi et al., 1995) but it is also a key element in the production of Ni–Mn–Co (NMC) cathode active materials for lithium-ion batteries (LIBs). The global demand for battery chemicals is currently increasing due to the trends of digitization and electrification of vehicles. Zn is also used in battery manufacturing although its primary uses are in corrosion protection, manufacturing of die castings and in the production of brass (Goodwin et al., 1998; Brodd et al., 1992). Anode sludges from Zn electrowinning usually contain around 40 wt% Mn and 6–10 wt% Pb on a dry basis (Kauppinen et al., 2020; Ayala and Fernández, 2013; Zhang et al., 2018). The presence of Zn, Ca, Mg, Na, K and Sr in the sludges at lower than 10 wt% total concentration has been reported; there may also be other base metals in tiny amounts (0.1 % or less each) (Kauppinen et al., 2020; Ayala and Fernández, 2013; Zhang et al., 2018). Aside from Zn electrowinning, Mn-bearing anode sludges are also formed during

electrolytic refining of Cu and Mn (Zhang and Cheng, 2007; Wang et al., 2019). Because of their significant Mn content, the anode sludges are acknowledged as secondary sources of Mn.

Zhang and Cheng (2007) have published a comprehensive review of the leaching methods for Mn-containing ores and secondary raw materials. Recently, Kauppinen et al. (2020) applied reductive H₂SO₄ leaching for Zn electrowinning sludges to liberate Mn. The recovery of Mn is high (98.5 %) but leaching of the impurities from such heterogeneous raw materials can rarely be completely avoided. Therefore, the leachates usually require further purification using methods such as solvent extraction, precipitation, adsorption or ion exchange. The impurity levels in the recovered Mn should be as low as possible for re-use applications such as battery manufacturing or the production of metallic Mn. Impurities may be allowed at ppm levels but the tolerable ranges are process- and element-specific (Qina et al., 2015; Krüger et al., 2014; Eilers-Rethwisch et al., 2018; Zhao et al., 2015; Lu et al., 2014; Louis et al., 1859).

The literature on the separation of Mn and Zn in sulfate solutions by

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solvent extraction (Ibiapina et al., 2018; Chen et al., ; Tanong et al., 2017; Biswas et al., 2016; Mishra et al., 2016; Haghighi et al., 2015; Falco et al., 2014; Nayl et al., 2014; Innocenzi and Veglio, 2012; Ahmadipour et al., 2011; Hosseini et al., 2011; Hosseini et al., 2010; Cheng et al., 2010; Lee et al., 2010; Pereira et al., 2007; El-Nadi et al., 2007; Nathsarma and Devi, 2006; Salgado et al., 2003; Cheng, 2000; Devi et al., 1997; Steiner et al., 1992) is summarized in a table that can be found in the electronic supplementary material (ESM). Bis(2,4,4-trimethylpentyl)phosphinic acid (BTMPPA, Cyanex 272) and bis-2-ethylhexyl hydrogen phosphate (D2EHPA) and their Na-salts are the most widely applied reagents (Lee et al., 2010; Pereira et al., 2007; Chen et al., ; Tanong et al., 2017; Biswas et al., 2016; Mishra et al., 2016; Haghighi et al., 2015; Falco et al., 2014; Nayl et al., 2014; Innocenzi and Veglio, 2012; Ahmadipour et al., 2011; Hosseini et al., 2011; Hosseini et al., 2010; Nathsarma and Devi, 2006; Salgado et al., 2003; Cheng, 2000; Devi et al., 1997). 2-ethylhexoxy(2-ethylhexyl)phosphinic acid (PC88-A, Ionquest 801, P-507) is structurally similar to BTMPPA and has qualitatively similar separation characteristics in the extraction of Mn and Zn (Biswas et al., 2016; Nathsarma and Devi, 2006). The use of bis(2,4,4-trimethylpentyl)thiophosphinic acid (Cyanex 302) (Biswas et al., 2016; Hosseini et al., 2011; Hosseini et al., 2010) and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) (Biswas et al., 2016; El-Nadi et al., 2007; Steiner et al., 1992) has also been studied for Mn–Zn separation but their industrial use is limited by their tendency to decompose (Flett, 2005). Furthermore, Cyanex 301 is known for its irreversible extraction of Fe and Cu (Steiner et al., 1992; Flett, 2005). Additionally, the complete stripping of Zn from loaded Cyanex 301 is cumbersome since it requires multiple contacts with concentrated acids (e.g. 5 N HCl or 30 % H₂SO₄) (Nayl et al., 2014; Steiner et al., 1992). A synergistic mixture of 0.5 M neodecanoic acid (Versatic 10) and 0.4 M 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63) was suggested by Cheng et al. (2010) for the separation of Co and Zn from Mn, Mg, and Ca. However, extraction of Zn using Versatic 10, or the synergistic mixture requires significantly higher pH than D2EHPA or BTMPPA. The pH₅₀ value for the extraction of Zn with the synergistic mixture was 3.8 (Cheng et al., 2010) whereas the corresponding pH₅₀ is usually below 2.5 with both D2EHPA and BTMPPA at similar extractant concentrations (Biswas et al., 2016; Ahmadipour et al., 2011; Hosseini et al., 2010; Lee et al., 2010; Pereira et al., 2007; Salgado et al., 2003). Tri-*n*-butyl phosphate (TBP) and trialkyl phosphine oxides (e.g. Cyanex 923) can be used to extract Zn from H₂SO₄ solutions when the free acidity in the aqueous phase is sufficiently high, e.g. free [H⁺] = 5 M or higher for extraction with TBP or between 0.1 and 1 M with Cyanex 923, respectively (Ibiapina et al., 2018). On the other hand, H₂SO₄ acts as an antisolvent for concentrated MnSO₄ solutions, such as the anode sludge leachates obtained by reductive H₂SO₄ leaching (Taylor, 1952). Therefore, NOPCs can be recommended only as phase modifiers or synergists in the treatment of very concentrated MnSO₄ solutions by solvent extraction.

Sulfate solutions with less than 45 g L⁻¹ Mn have been widely studied in earlier solvent extraction research on Zn–Mn separation (Ibiapina et al., 2018; Chen et al., ; Tanong et al., 2017; Biswas et al., 2016; Mishra et al., 2016; Haghighi et al., 2015; Falco et al., 2014; Nayl et al., 2014; Innocenzi and Veglio, 2012; Ahmadipour et al., 2011; Hosseini et al., 2011; Hosseini et al., 2010; Cheng et al., 2010; Lee et al., 2010; Pereira et al., 2007; El-Nadi et al., 2007; Nathsarma and Devi, 2006; Salgado et al., 2003; Cheng, 2000; Devi et al., 1997; Steiner et al., 1992; Flett, 2005; Pakarinen and Paatero, 2011; MOHAPATRA et al., 2007; Principe and Demopoulos, 2004). Extraction of Mn to the organic phase, followed by stripping of a Mn-rich product (Pakarinen and Paatero, 2011) is a viable process scheme for solutions with low or moderate Mn content. However, a different approach was investigated in this study for the highly concentrated ([Mn] > 150 g L⁻¹) MnSO₄ solutions. The aim was to extract Al, Ca, Fe and Zn to the organic phase while minimizing the extraction of Mn. Usually, Al, Ca, Fe and Zn are extracted by D2EHPA at a lower pH than Mn (Lee et al., 2010; Pereira et al., 2007;

Cheng, 2000; Pakarinen and Paatero, 2011; MOHAPATRA et al., 2007; Principe and Demopoulos, 2004). Since the impurity metals (here, metals other than Mn) are present in the anode sludge leachate at much smaller concentration than Mn, extraction of the impurities should be possible with smaller chemical consumption than extraction and stripping of Mn. However, changes in temperature or composition of the feed solutions affect the distribution coefficients and might even change the extraction order of the metals for D2EHPA (Lee et al., 2010; Pereira et al., 2007; Cheng, 2000). BTMPPA also extracts Al, Fe, and Zn ahead of Mn (Flett, 2005; Pakarinen and Paatero, 2011; MOHAPATRA et al., 2007), but extraction of Ca is negligible at pH values below 5; Mn is extracted ahead of Ca (Pakarinen and Paatero, 2011). Besides the differences in chemical equilibria with chemically different solutions, the physical behavior of the phases at high ionic strength is different than at low or moderate ionic strength. Adjusting the pH of concentrated MnSO₄ solutions is restricted, since addition of alkali metal hydroxides or NH₃ in large quantities may result in the formation of Tutton's salts (Montgomery et al., 1966).

Based on the literature discussed above, D2EHPA and BTMPPA were selected as extractants for removal of Zn and Fe from concentrated MnSO₄ solution in this study. Results from the separation of Mn and Zn by continuous multi-stage extraction have been published earlier by only a few authors. Haghighi et al. (2015) and Nathsarma and Devi (2006) have simulated the countercurrent extraction of Mn- and Zn-bearing solutions by batch experiments. Salgado et al. (2003) included two-stage crosscurrent extraction in their studies. Also, Pereira et al. (2007) have published results from continuous countercurrent separation of Mn and Zn. This paper contributes to the topic by presenting new extraction equilibria and results of the purification of Mn-rich anode sludge leachate by continuous countercurrent solvent extraction in laboratory-scale mixer-settlers.

2. Materials and methods

2.1. Production of the MnSO₄ solutions

MnSO₄ solutions were prepared for the solvent extraction studies by leaching anode sludge from Zn electrowinning by the method described by Kauppinen et al. (2020). The leaching procedure was scaled up for a 50 dm³ glass reactor with a mixer and baffles made of acid-resistant steel (AISI 316) to produce enough feed solution for the continuous experiments. The sludge was first mixed for 1 h with 0.5 M H₂SO₄ (reagent grade 95–98 wt%, Merck KGaA) solution to wash most of the Mg, Al, Fe and Zn before liberation of Mn by reductive leaching. S/L of 500 g L⁻¹ was used in the preliminary washing step, and water was pre-heated to 65–70 °C before introducing the sludge and acid into the reactor. The acidic wash liquor was separated from the sludge by gravity settling. After removing most of the acidic overflow, the sludge was rinsed with pure water and the suspension was vacuum filtered in 5 dm³ Büchner funnels to yield the washed anode sludge. The moisture content of the sludge was 34 wt% after filtration.

In the reductive leaching step pure water and part of the washed anode sludge were pre-loaded into the reactor. 95 wt% H₂SO₄ (Orikem Oy, Kangasala, Finland) and 30 wt% H₂O₂ (VWR Chemicals) were continuously fed into the reactor by peristaltic pumps. The flowrates were 22.8 mL min⁻¹ and 41.3 mL min⁻¹ for H₂SO₄ and H₂O₂, respectively. To maintain the S/L ratio at 450 g L⁻¹ during the leaching process, the rest of the wet sludge was intermittently fed into the reactor at a rate of 5.4 kg h⁻¹. A few drops of anionic polyacrylamide flocculant (1 g L⁻¹ solution of Kemira Superfloc A-100) were added into 40 dm³ of suspension to aid the solid–liquid separation after the reductive leaching. The preliminary wash and leaching before solvent extraction are depicted in Fig. 1.

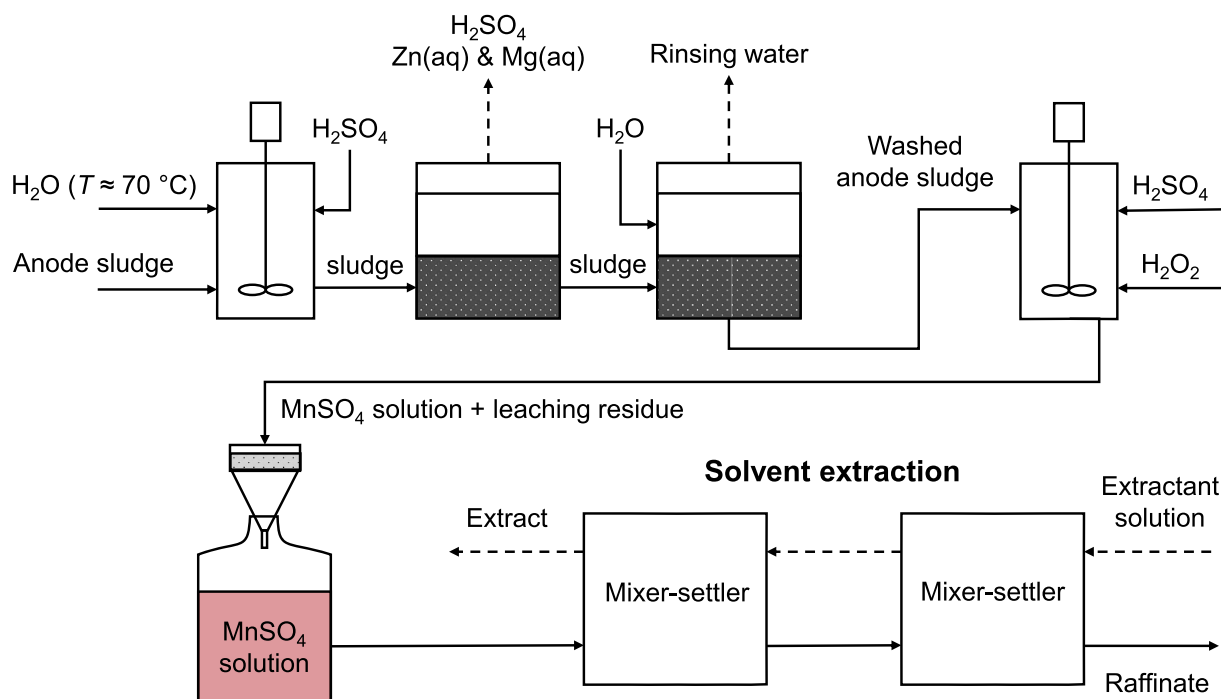


Fig. 1. Schematics showing the processing of the anode sludge in this study.

2.2. Batch extraction experiments

D2EHPA (97 % bis(2-ethylhexyl) hydrogen phosphate, Merck KGaA) and BTMPPA (85–90 % bis(2,4,4-trimethylpentyl)phosphinic acid, trade name Cyanex 272, Solvay) were diluted in Exxsol D80 (Exxon Mobil) aliphatic hydrocarbon mixture, and the solutions were used without pre-treatments. The metal concentrations of the anode sludge leachate used in the batch experiments are given in Table 1. The total concentration of Co, Ni and Cu together was 5.4 mg L^{-1} . The pH of the solution was 0.6 and the redox potential was $+800 \text{ mV}$ (vs. SHE) at $22 \pm 1 \text{ }^\circ\text{C}$. This solution is referred as the “Pregnant leach solution 1 (PLS 1).”

Batch extractions were carried out in a 1 dm^3 jacketed glass reactor. The pH was adjusted by bubbling gaseous NH_3 into the reaction mixture via a submerged PTFE tube. The temperature was controlled by an external thermostat. Volumetric phase ratio $\text{O/A} = 1$ was used in determination of the pH isotherms. Loading isotherms were determined in a similar manner, but the O/A ratio was varied, whereas the pH was maintained constant. Back-extraction performance was studied by stripping loaded 0.8 M extractants with $0.5 \text{ M H}_2\text{SO}_4$ at various O/A ratios without other pH adjustment. The equilibration time was 15 min.

2.3. Continuous experiments

Composition of the feed solution in the continuous experiments (Table 2) was slightly different from PLS 1 due to the scale-up of the

Table 1

Metal concentrations in the first anode sludge leachate (PLS 1) as determined from ten different analyses of parallel samples.

Element	Unit	Average	Standard deviation
Mn	g L^{-1}	179.8	11.3
Al	mg L^{-1}	82.7	29.3
K	mg L^{-1}	4121.4	168.3
Ca	mg L^{-1}	290.8	127.1
Fe	mg L^{-1}	37.5	5.4
Zn	mg L^{-1}	448.6	13.6

Table 2

Metal concentrations in the second anode sludge leachate (PLS 2) as determined from nine different analyses of parallel samples.

Element	Unit	Average	Standard deviation
Mn	g L^{-1}	161	9.1
Na	g L^{-1}	17.7	2.4
Mg	mg L^{-1}	215.1	9.6
Al	mg L^{-1}	63	45.7
K	mg L^{-1}	2997	280.9
Ca	mg L^{-1}	203.7	42.9
Fe	mg L^{-1}	134.9	12.4
Zn	mg L^{-1}	999.4	41.5

reductive leaching and subsequent solid–liquid separation. The leachate used in the continuous experiments (PLS 2) was more acidic ($\text{pH} < 0$), and the total concentration of Co, Ni and Cu together in the solution was 12.1 mg L^{-1} . The redox potential of the second leachate (PLS 2) was $+760 \text{ mV}$ (vs. SHE) at $22 \pm 1 \text{ }^\circ\text{C}$ after pH adjustment to 1.2.

MEAB MSU0,5 mixer-settler units (MEAB) made of PTFE and PFA were used in the continuous extraction experiments. The mixer volume of a single MSU0,5 unit is 120 mL; the volume of the settler is 460 mL. The horizontal cross-sectional area of the settler is 55 cm^2 . PLS 2 and the extractant solutions were fed by PTFE diaphragm pumps (ProMinent DLTA). A dual-channel syringe pump (Gemini 88, KD Scientific) was used for pH adjustment with NaOH or H_2SO_4 . Additionally, a Consort C3060 was used for pH logging. All continuous experiments were done at room temperature ($22 \pm 1 \text{ }^\circ\text{C}$). A minimum of five cascade volumes of liquid were processed in each experiment as suggested by the conventional theory on residence time distributions. 3.6 min mean residence time in mixer (τ_{mix}) was near the lower operating limit determined by the linear settling velocity and horizontal cross-sectional area of the settlers. D2EHPA and BTMPPA solutions were prepared with 0.8 M nominal concentration of the active component. The proton capacities of the D2EHPA and BTMPPA solutions were 0.779 mol L^{-1} and 0.755 mol L^{-1} , respectively, as determined by titrating the extractant solutions in 75 vol-% isopropanol against 0.1 M NaOH standard solution. The 0.8 M extractant solutions were pre-neutralized using 5 M NaOH at $\text{O/A} =$

10 before extraction. The prepared Na-BTMPPA was a completely transparent single phase microemulsion, whereas the D2EHPA solution and 5 M NaOH formed a milky dispersion, which was continuously mixed in the feed tank to maintain homogeneity. The solvent-to-feed flow ratios (S/F) reported here are given for the volumetric flow-rates of the pre-neutralized extractants. Nominal concentrations (0.8 M) of the active component are used in discussion of the pre-neutralized extractant solutions.

2.4. Analyses of the liquid samples

The organic samples were backextracted at A/O = 20 with HCl (GPR RECTAPUR, VWR). The HCl raffinate from backextraction were analyzed using ICP-MS (Agilent 7900). 3 N HCl was used for the organic samples from the batch experiments, while 5 N HCl was used for the samples from the continuous experiments. It was realized during the experimental work that stripping of Fe from loaded D2EHPA would be most efficient by 5 N HCl, whereas 3–5 M H₂SO₄ should be used for the stripping of BTMPPA (Sandhibigraha et al., 2000). To get reliable information about the Fe loading in the continuous extraction, certain organic steady-state samples were dissolved in super-pure HNO₃ (67–69 wt%, ROMIL) by wet digestion (Milestone UltraWAVE) under 250 °C and 130 bar for 10 min after a 70 min heating ramp. Metal concentrations in the aqueous samples were analyzed using ICP-MS.

2.5. Data treatment

The selectivity of Zn and Fe over Mn was evaluated by comparing the molar concentration of Mn in the organic phase against the total molar concentration of metals in the organic phase. The total concentration of metals in the organic phase was approximated as the sum of [Fe]_{org}, [Zn]_{org}, and [Mn]_{org}, since the concentrations of other metals in the organic samples were negligible with respect to [Fe]_{org}, [Zn]_{org} and [Mn]_{org}. The formal mole fraction of Mn in the organic phase was defined using Eq. (1),

$$f_{Mn,org}^* = \frac{[Mn]_{org}}{[M]_{org,tot}} \approx \frac{[Mn]_{org}}{[Fe]_{org} + [Zn]_{org} + [Mn]_{org}} \quad (1)$$

where $f_{Mn,org}^*$ is the mole fraction of Mn in the organic phase with respect to the total concentration of metals in the organic phase and $[M]_{org,tot}$ is the total concentration of metals in the organic phase [mol L⁻¹].

The crowding plots, where quantity $f_{Mn,org}^*$ is plotted against $[M]_{org,tot}$ or O/A were convenient for selectivity evaluations because, in this case, [Fe] in the aqueous phase was lowered below the detection limit and distribution coefficients or separation factors could not be calculated for Fe. Furthermore, the raffinates from backextraction analyses (see chapter 2.5) of the organic samples were less prone to interference-related analytical errors due to their much lower salinity compared to the aqueous samples with $[Mn] \geq 150 \text{ g L}^{-1}$.

The relative purity of Mn was calculated using Eq. (2),

$$P_R(Mn) = \frac{w_{Mn}}{\sum_j w_j} \quad (2)$$

where $P_R(Mn)$ is the relative purity of Mn [wt%], w is the mass concentration [g L⁻¹] and the summation in the denominator goes through all metals in the solution.

The reported average pH values for the continuous experiments were determined from the pH logger data by taking the average of the pH values from the end half of an experiment (Fig. 2) to exclude the fluctuations in the startup-phase. Similarly, the reported extract and raffinate concentrations (Table 3) are the average concentration from the last three samples.

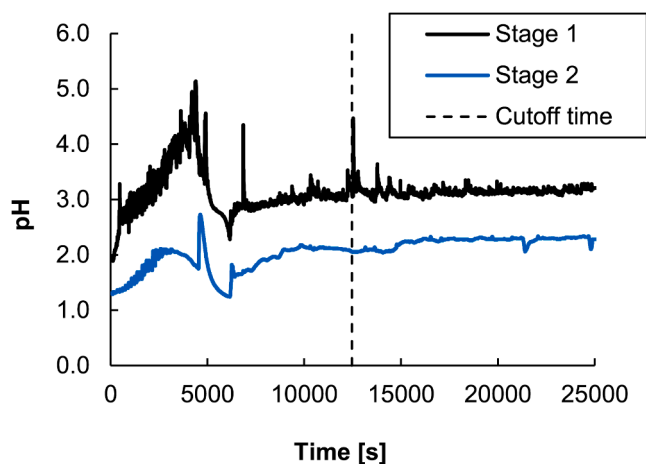


Fig. 2. Stagewise pH profiles from two-stage continuous countercurrent extraction of the anode sludge leachate (PLS 2) with 0.8 M Na-D2EHPA as an example to illustrate the determination of the average pH values.

3. Results and discussion

3.1. Comparison of the performances of D2EHPA and BTMPPA in batch extractions

3.1.1. Effect of pH and extractant concentration on extraction of Fe, Zn and Mn

Fe and Zn were efficiently removed from the concentrated MnSO₄ leachate (Fig. 3) at pH 3.0 and above. As a more acidic reagent, D2EHPA can extract the metals at lower pH values than BTMPPA (Pakarinen and Paatero, 2011). Over 80 % of Fe was extracted by 0.2 M D2EHPA at pH 0.8, whereas a pH > 1.5 was required with 0.2 M BTMPPA. The interpolated pH₅₀ values of Zn extraction were 1.48 and 2.12 for 0.2 M D2EHPA and 0.2 M BTMPPA, respectively. The effect of pH on the extraction of Zn (Fig. 3) was qualitatively similar with earlier results published in the literature (Chen et al.; Biswas et al., 2016; Innocenzi and Veglio, 2012; Pereira et al., 2007; Salgado et al., 2003; Cheng, 2000). An increase in extractant concentration decreased the pH required to achieve a specific degree of Zn extraction (Fig. 3), in accordance with Pereira's et al. (2007) observations. Extraction of Mn by 0.8 M BTMPPA was 1.9–5.8 % and 3.3–11.4 % by 0.8 M D2EHPA as determined from the raffinate phase concentrations (Fig. 3). The extraction of Co, Ni and Cu could not be verified from the analytical results, likely due to their very low initial concentration (below 5 mg L⁻¹ each) in PLS 1 (Table 1). The concentration of Al in the organic samples throughout this study was below 20 mg L⁻¹, meaning that Al was only weakly extracted ($E(Al) < 30 \%$) by both extractants.

3.1.2. Extraction of Ca

The extraction of Ca by both BTMPPA and D2EHPA was negligible between pH 0.5 and 6 (Fig. 4). The concentration of Ca was below the detection limit (approximately 25 mg L⁻¹) in almost all the organic samples from determination of the loading isotherms (Fig. 5). For D2EHPA, this is an unexpected result when compared to earlier studies for different solutions containing Ca. Haghghi et al. (2015) reported significant extraction of Ca by 30 vol-% D2EHPA for various O/A ratios at 45 °C, Cheng (2000) obtained over 1 g L⁻¹ loading of Ca with 10 vol-% D2EHPA with around 250 mg L⁻¹ of Ca in the aqueous phase in equilibrium. Additionally, Pakarinen and Paatero (2011) reported over 80 % extraction of Ca by 25 vol-% D2EHPA at pH ≥ 2.5 and 25 °C from 200 mg L⁻¹ initial concentration. Extractions with 0.2 M extractant solutions were repeated at 15 °C, since Pakarinen and Paatero (2011) have observed an increase in the extraction of Ca at lowered temperature.

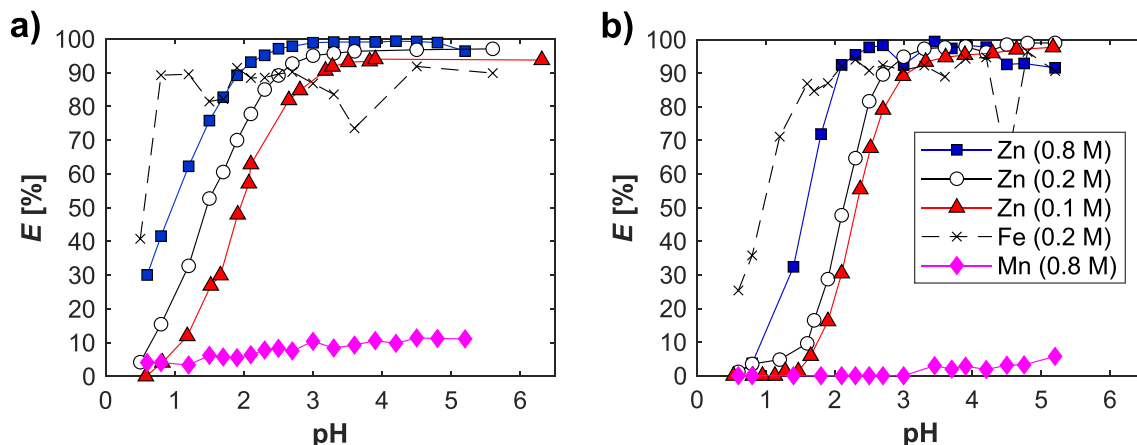


Fig. 3. Effect of pH on extraction of Zn, Fe and Mn at various extractant concentrations at 25 ± 1 °C by a) D2EHPA and b) BTMPPA from the anode sludge leachate. Concentration of the extractant is given in brackets. $[Zn]_0 = 450$ mg L⁻¹, $[Fe]_0 = 40$ mg L⁻¹, $[Ca]_0 = 320$ – 350 mg L⁻¹ and $[Mn]_0 = 180$ g L⁻¹.

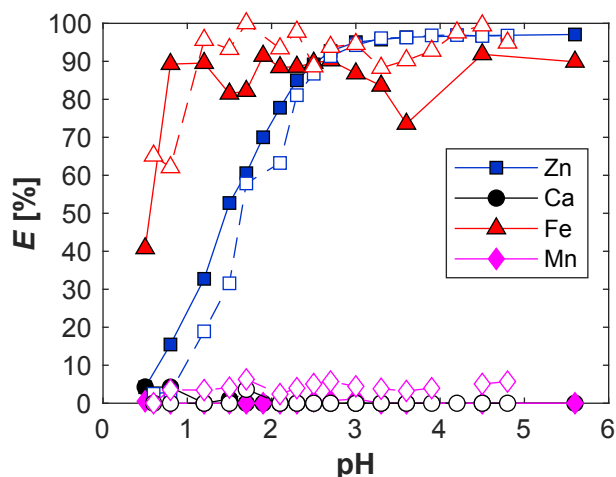


Fig. 4. Extraction of Zn, Fe, Ca and Mn by 0.2 M D2EHPA at 25 °C (filled symbols) and 15 °C (hollow symbols) from the anode sludge leachate. $[Zn]_0 = 450$ mg L⁻¹, $[Fe]_0 = 40$ mg L⁻¹, $[Ca]_0 = 320$ – 350 mg L⁻¹ and $[Mn]_0 = 180$ g L⁻¹.

Here Ca was not extracted, even at 15 °C. Lowering the temperature from 25 °C to 15 °C did not have a significant effect on the extraction of Zn, Fe and Mn, either (Fig. 4). The reason behind the poor Ca extraction by D2EHPA was not studied further, but it seems to be associated with the high amount of Mn and/or SO₄²⁻ in the system.

3.1.3. Effect of metal loading in the organic phase on Zn/Mn and Fe/Mn selectivity

The fraction of Mn in the organic phase decreased with both extractants when the metal loading in the organic phase increased (Fig. 6 a) regardless of the pH or temperature used in the experiment. Selectivity towards Zn and Fe was higher with BTMPPA than with D2EHPA. The lowest $f_{Mn,org}^*$ was 28.9 mol-% for crowded D2EHPA at 0.2 M extractant concentration and pH 2.7, whereas with crowded 0.2 M BTMPPA the $f_{Mn,org}^*$ was 10.0 mol-%, respectively. The Mn-selectivity of D2EHPA was affected by pH (Fig. 6). Crowding of 0.8 M D2EHPA at pH 3.0 lowered the $f_{Mn,org}^*$ to 35 mol-%. But, at pH 1.7, the $f_{Mn,org}^*$ in loaded D2EHPA did not decrease below 65 mol-%. On the other hand,

$f_{Mn,org}^*$ in the crowded 0.8 M BTMPPA lowered below 10 mol-% at pH 1.7. Co-extraction of Mn can thus be limited by crowding the extractants (Fig. 6 b). Mn ions that occupy the deprotonated organic ligands are replaced by Zn and Fe ions; the separation can also be carried out using low pH and high excess of BTMPPA. The aqueous solution can then be maintained at low pH, and the risk of precipitation due to pH elevation will be lower. However, choosing the extractant and operating conditions is not unequivocal since, at low pH, D2EHPA extracts higher overall amounts of Zn and Fe than BTMPPA does.

3.1.4. Separation of the co-extracted Mn from Zn and Fe during backextraction

The co-extracted Mn was recovered at 99.5–99.8 wt% relative purity by stripping the loaded 0.8 M extractants with 0.5 M H₂SO₄ at high O/A ratios (Fig. 7). The Mn-rich fractions of the stripping raffinate contained 29.4–33.9 g L⁻¹ Mn, 13–16 mg L⁻¹ Al, 1.5–5.2 mg L⁻¹ Zn and < 1 mg L⁻¹ Fe. 55.7 % of the co-extracted Mn could be selectively stripped at $P_R(Mn) > 99.5$ wt% from D2EHPA and 71.5 % from BTMPPA, respectively. Increasing the amount of stripping acid (i.e. lowering O/A and/or increasing the concentration of H₂SO₄) lowers the pH so that Zn and Fe are also stripped according to the pH isotherms (Fig. 3). Thus, the relative purity of Mn was lowered with decreasing O/A (Fig. 7). Zn and Mn can be completely stripped from BTMPPA and D2EHPA with adequate amounts of H₂SO₄ or HCl (Biswas et al., 2016). However, stripping Fe from BTMPPA and D2EHPA requires special attention. Fe (III) is only partially stripped from loaded D2EHPA by H₂SO₄, but 99 % of the loaded Fe can be stripped by 5 N HCl (Sandhibigraha et al., 2000). Moreover, stripping by 7.5 % oxalic acid at 60 °C (Singh et al., 2013) or a mixture of H₂SO₄ and a reducing agent (Liu et al., 2014) has been suggested for a complete Fe stripping from D2EHPA. Fe is more efficiently stripped from BTMPPA by H₂SO₄ than by HCl; 98–100 % Fe stripping can be obtained with 8–10 N H₂SO₄ (Sandhibigraha et al., 2000). Stripping of Fe with HCl from BTMPPA is inefficient with over 3 N concentrations (Sandhibigraha et al., 2000). Fe can be removed from the solution by hydroxide precipitation before extraction, or a bleed stream for Fe removal could be employed to the solvent extraction process.

3.2. Extraction performance in continuous counter-current extraction

3.2.1. Removal rates of Zn, Fe and Mn

Table 3 summarizes the removal percentages of Zn, Fe and Mn from

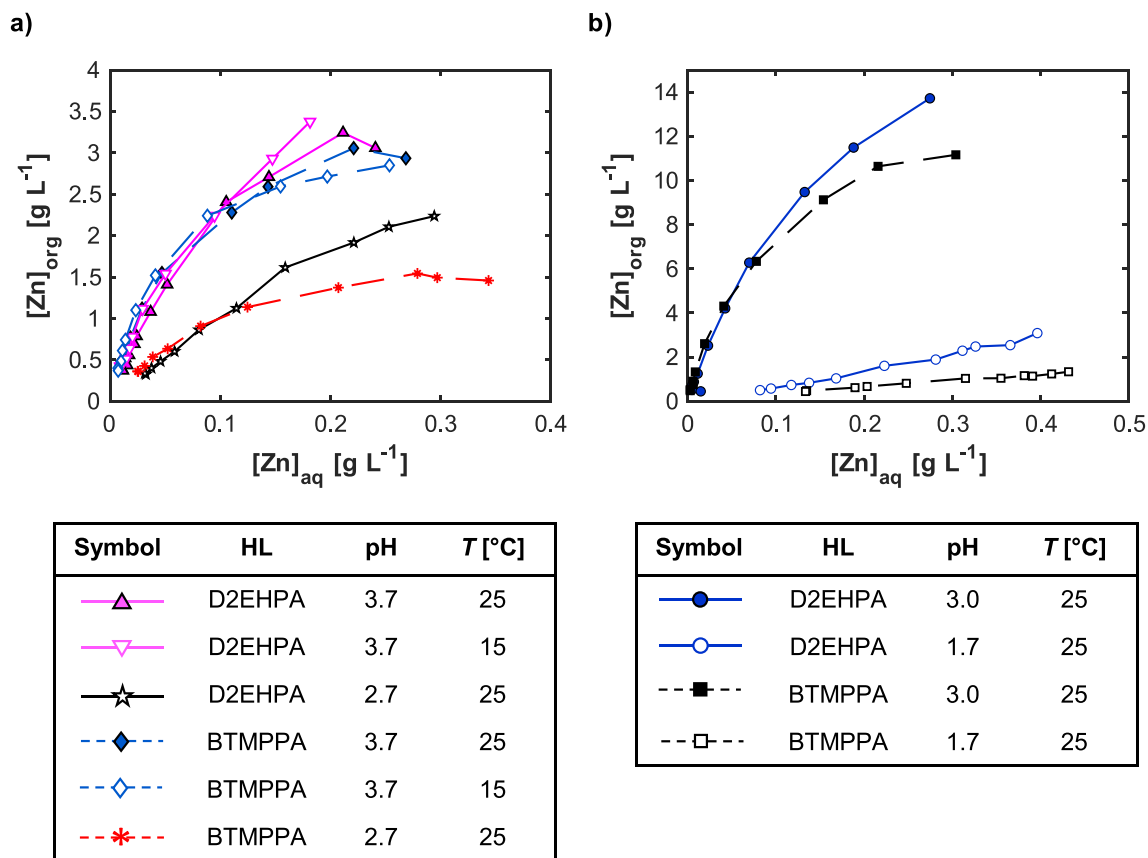


Fig. 5. The determined Zn loading isotherms for a) 0.2 M and b) 0.8 M extractants. $[Zn]_0 = 450 \text{ mg L}^{-1}$, $[Fe]_0 = 40 \text{ mg L}^{-1}$, $[Ca]_0 = 320\text{--}350 \text{ mg L}^{-1}$ and $[Mn]_0 = 180 \text{ g L}^{-1}$; HL denotes extractant.

the anode sludge leachate in the continuous experiments. D2EHPA removed Zn and Fe more efficiently than BTMPPA did, but it co-extracted more Mn. Single-stage extraction with 0.8 M Na-D2EHPA at $22 \pm 1 \text{ }^\circ\text{C}$ with a 3.6 min mean residence time (τ_{mix}) and $S/F = 1$ removed 97 % of the Fe, 96 % of the Zn and 16.6 % of the Mn. In similar conditions, 0.8 M Na-BTMPPA removed 77.1 % of the Fe, 93.1 % of the Zn and 8.4 % of the Mn. The addition of another extraction stage as well as lowering the S/F ratio to 0.43 increased the removal of Zn and Fe by D2EHPA and decreased the removal of Mn. Two-stage extraction by BTMPPA was more sensitive to pH adjustment. When pH was adjusted in the aqueous feed stage (stage 1) only, the raffinate from two-stage extraction ($S/F = 0.43$; $\tau_{\text{mix}} = 3.6 \text{ min}$) by 0.8 M Na-BTMPPA had a higher Zn concentration (96.3 mg L^{-1}) than the raffinate from single-stage extraction ($S/F = 1$) (69.8 mg L^{-1}). Introducing the pH adjustment in both extraction stages resulted in 99.5 % Zn removal and 98.7 % Fe removal by 0.8 M Na-BTMPPA; also, the Mn loading in the organic phase increased (Table 3). However, the concentration of Mn in loaded BTMPPA ($<4 \text{ g L}^{-1}$) was still significantly lower than that in loaded D2EHPA ($>9 \text{ g L}^{-1}$) although the extraction efficiencies of Zn and Fe were similar.

3.2.2. Comparison of the experimental results against theoretical predictions

The experimental results are in relatively good agreement with the McCabe–Thiele predictions (Fig. 8 a–d) of the extraction of Zn. Loading

isotherms of 0.8 M BTMPPA and 0.8 M D2EHPA at $\text{pH} = 3$ are so similar that there is no significant difference between the predictions (Fig. 8 a & c). Moreover, the Zn extraction equilibria and the McCabe–Thiele diagrams (Fig. 8 e–f) suggest that 2 stages operating at $O/A = 0.4$ and $\text{pH} = 3$ would be sufficient for the treatment of a more concentrated solution with e.g. 4 g L^{-1} Zn without significant loss of purification performance. However, relatively large errors to the predicted stagewise concentrations can be introduced by fitting, interpolation or extrapolation of steep equilibrium curves. Even a small difference in raffinate concentration corresponds to a relatively large change in extract concentration. The average concentrations given in Table 3 are not in complete agreement with mass balance; the errors can be explained by the deviations in the ICP-MS analyses, precipitation and fluctuation in the feed flowrates.

3.2.3. Effect of the mean residence time on process performance

Increasing mean residence time from 3.6 min to 6.0 min in the two-stage countercurrent extraction increased the Zn/Mn and Fe/Mn selectivities for 0.8 M Na-BTMPPA considerably (Table 4). The increase in τ_{mix} from 3.6 min to 6.0 min had marginal—if any—effect on the extraction performance of D2EHPA. Higher Zn and Fe loading was obtained with $\tau_{\text{mix}} = 6.0 \text{ min}$ than with $\tau_{\text{mix}} = 3.6 \text{ min}$. However, the pH differed slightly between these experiments, which could explain the observed difference in extraction performance. Adjusting the pH on both stages in the two-stage extraction by 0.8 M Na-D2EHPA increased the extraction of Mn but had very little effect on removal of Zn and Fe.

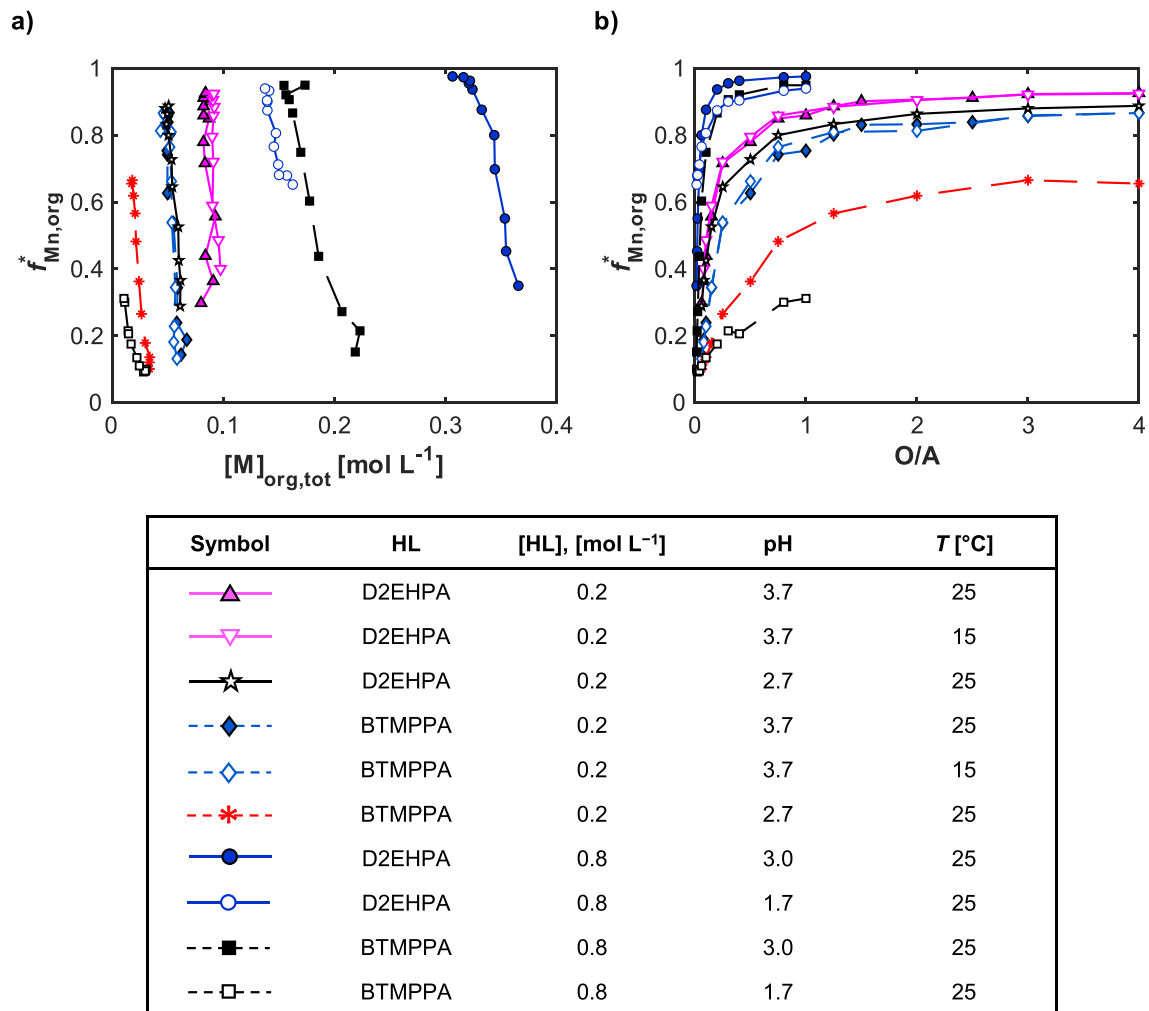


Fig. 6. Effect of crowding on the mole fraction of Mn in the organic phase. $[Zn]_0 = 450 \text{ mg L}^{-1}$, $[Fe]_0 = 40 \text{ mg L}^{-1}$, $[Ca]_0 = 320\text{--}350 \text{ mg L}^{-1}$ and $[Mn]_0 = 180 \text{ g L}^{-1}$. HL denotes extractant and $f_{Mn,org}^*$ is defined in Eq. (1).

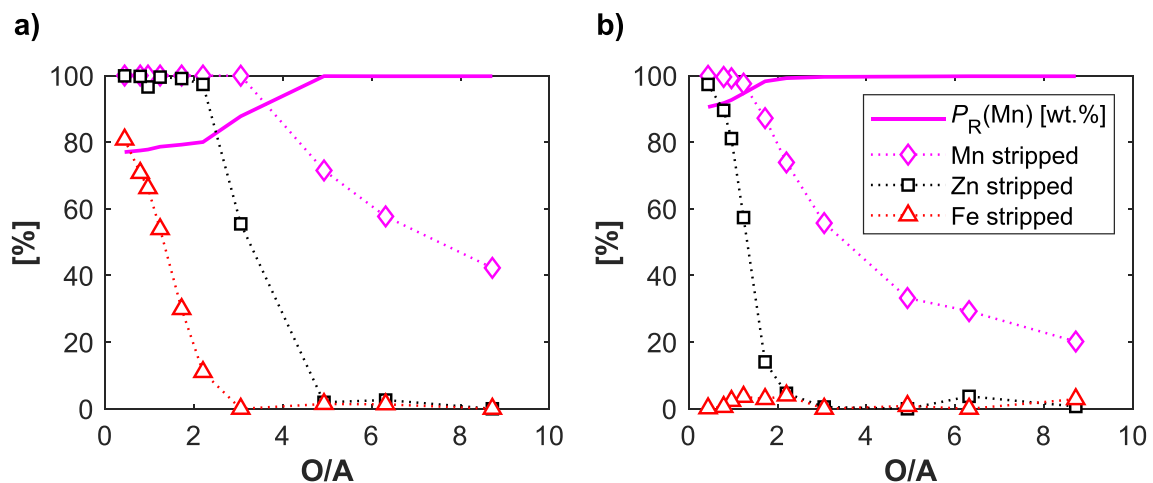


Fig. 7. Effect of phase ratio on stripping of Mn, Zn and Fe from loaded 0.8 M BTMPPA (a) and 0.8 M D2EHPA (b) at $25 \pm 1 \text{ }^\circ\text{C}$ with 0.5 M H_2SO_4 . Initial metal loadings: $[Mn]_{BTMPPA} = 8.2 \text{ g L}^{-1}$, $[Zn]_{BTMPPA} = 1.09 \text{ g L}^{-1}$, $[Fe]_{BTMPPA} = 79.9 \text{ mg L}^{-1}$; $[Mn]_{D2EHPA} = 16.8 \text{ g L}^{-1}$, $[Zn]_{D2EHPA} = 1.09 \text{ g L}^{-1}$, $[Fe]_{D2EHPA} = 76.4 \text{ mg L}^{-1}$.

Therefore, with 0.8 M D2EHPA the second extraction stage can operate at $\text{pH} \approx 2$ and almost complete removal of Zn and Fe is obtained for the anode sludge leachates studied (Table 3). High extraction of Zn is typical for both D2EHPA and BTMPPA. The Zn removal reported here for D2EHPA is similar to the results of Pereira et al. (2007): they obtained over 98 % Zn removal by 20 wt% D2EHPA in three countercurrent extraction stages at $\text{pH} = 2.5$ and 28 ± 1 °C. However, a significant difference in the extraction of Fe between this study and Pereira et al. (2007) can be observed. The concentration of Fe has decreased from 240.6 mg L^{-1} to 115.5 mg L^{-1} in the three-stage extraction with $S/F = 1$ in Pereira et al. (2007), whereas, in the current study, [Fe] was lowered from 135 mg L^{-1} to below 2 mg L^{-1} in two extraction stages with $S/F = 0.43$. Moreover, the results of Pereira et al. (2007) show a 22 % and an 11.3 % decrease in concentrations of Ca and Mg, respectively. However, the concentrations of Ca and Mg in their feed solution were roughly 2.5 and 10 times higher, respectively, than in the PLS 2 solution studied here (Table 2). Ca could not be detected in the organic samples during this work. Mg was not detected in loaded BTMPPA, either. The concentration of Mg in all D2EHPA samples from the countercurrent extractions was below 2 mg L^{-1} . The 7–9 % removal of Mn reported in this study (Table 3) for two-stage extraction by 0.8 M Na-D2EHPA is similar to the 8.3 % Mn removal obtained by Pereira et al. (2007), although the concentration of Mn in the aqueous feed solution was much lower ($<1 \text{ g L}^{-1}$) in Pereira et al. (2007).

3.2.4. Formation of solids

Solid precipitates were formed during the countercurrent extractions. These precipitates caused gelation in the settlers. However, no precipitates were visually observed in the extract and raffinate samples or during the batch extraction experiments. The precipitates were likely Mn and Fe hydroxides, but the formation of Tutton's salts is also possible. Operation of the solvent extraction process discussed here is recommended with a high excess of extractant. Thus, the active amount of extractant would be sufficiently high for the desired extraction efficiency at the lowest possible pH (Fig. 3). The precipitation can perhaps be completely avoided at low pH. On the other hand, an increase in extractant concentration or S/F ratio likely increases co-extraction of Mn. However, avoiding precipitation is a priority over avoiding extraction of Mn because a significant amount of the co-extracted Mn

Table 3

Removal percentages of Zn, Fe and Mn and their average concentrations in the extracts and raffinates in continuous countercurrent solvent extraction of Mn-rich sulfate leachate with 0.8 M Na-BTMPPA and 0.8 M Na-D2EHPA at 22 ± 1 °C. Stages were numbered starting from the organic feed stage and ending in the aqueous feed stage. Average concentrations in the aqueous feed solutions are given in bold font.

Extractant	S/F	τ_{mix} min	pH_{avg} stage 1	pH_{avg} stage 2	[Mn]_{aq} g L⁻¹	[Zn]_{aq} mg L⁻¹	[Fe]_{aq} mg L⁻¹	[Mn]_{org} g L⁻¹	[Zn]_{org} mg L⁻¹	[Fe]_{org} mg L⁻¹	R(Mn) %	R(Zn) %	R(Fe) %
Na-BTMPPA	–	–	–	–	156.6	1005.4	133.7	–	–	–	–	–	–
	1	3.6	3.12 ^a (0.09 [*])	–	143.3	69.8	30.6	1.6	756.7	29.7	8.4	93.1	77.1
	0.43	3.6	3.65 ^a (0.06 [*])	2.15 ^u (0.05 [*])	147.8	96.3	9.9	1.6	2114.1	218.9	5.6	90.4	92.6
	0.43	3.6	3.07 ^a (0.14 [*])	2.91 ^a (0.29 [*])	148.4	5	1.7	3.8	2381	312.2	5.2	99.5	98.7
0.43	6	3.18 ^a (0.03 [*])	1.97 ^u (0.07 [*])	147.4	50.7	< 0.5	1.3	2330.8	298.5	5.8	95	100	
Na-D2EHPA	–	–	–	–	167.9	977.4	135.6	–	–	–	–	–	–
	1	3.6	2.85 ^a (0.02 [*])	–	140.1	39.2	4.1	12.3	948	85.1	16.6	96	97
	0.43	3.6	3.05 ^a (0.20 [*])	1.99 ^u (0.26 [*])	152.9	5.5	< 0.5	9.2	2217.8	229	8.9	99.4	100
	0.43	3.6	3.12 ^a (0.05 [*])	3.07 ^a (0.08 [*])	155.6	2.7	2.2	15.8	2481	306.2	7.3	99.7	98.4
0.43	6	3.14 ^a (0.07 [*])	2.24 ^u (0.09 [*])	155.7	1.4	< 0.5	9.3	2559.8	311.1	7.3	99.9	100	

*Standard deviation.

^{a)} adjusted pH.

^{u)} unadjusted pH.

Table 4

Selectivity ratios and total molar concentration of metals in the extracts from continuous countercurrent solvent extraction of Mn-rich sulfate leachate with 0.8 M Na-BTMPPA and 0.8 M Na-D2EHPA at 22 ± 1 °C. Total molar concentration of metals was approximated with $[\text{M}]_{\text{org,tot}} \approx [\text{Zn}]_{\text{org}} + [\text{Fe}]_{\text{org}} + [\text{Mn}]_{\text{org}}$.

Extractant	N	S/F	τ_{mix} min	$\frac{[\text{Zn}]_{\text{org}} + [\text{Fe}]_{\text{org}}}{[\text{Mn}]_{\text{org}}}$	$\frac{[\text{Mn}]_{\text{org}}}{[\text{M}]_{\text{org,tot}}}$	$[\text{M}]_{\text{org,tot}}$ mol L⁻¹
Na-BTMPPA	1	1	3.6	0.42	0.7	0.04
	2	0.43	3.6	1.27	0.44	0.06
	2*	0.43	3.6	0.61	0.62	0.11
Na-D2EHPA	2	0.43	6.0	1.77	0.36	0.06
	1	1	3.6	0.07	0.93	0.24
	2	0.43	3.6	0.23	0.82	0.21
2*	0.43	3.6	0.15	0.87	0.33	
2	0.43	6.0	0.27	0.79	0.21	

*pH adjustment in both stages.

can be selectively recovered in stripping (see chapter 3.1). The estimated Mn losses to the impure stripping fractions due to co-extraction were 0.1–0.3 % for BTMPPA and 1.2–2.1 % for D2EHPA (28.5 % and 44.3 % of the loaded Mn, respectively, Table 3).

3.3. Composition of the purified leachate

The average composition of the raffinates (Table 3) where $[\text{Zn}]_{\text{aq}} \leq 5 \text{ mg L}^{-1}$ is given in Table 5. The purified anode sludge leachate is proposed for use in the co-precipitation synthesis of NMC cathode precursors. The diluted concentrations for NMC622 and NMC811 in Table 5 are calculated for a solution in which the total concentration of Ni, Mn and Co is 2 mol L^{-1} , which is suitable for the hydroxide co-precipitation synthesis (Eilers-Rethwisch et al., 2018). Na and K are usually soluble in alkaline media. Therefore, Al, Mg, and Ca would be the most significant impurities for the co-precipitation synthesis at concentrations of 5.8–11.5 mg L^{-1} , 15–30 mg L^{-1} and 13–30 mg L^{-1} , respectively. The concentration of Zn and Fe will be lower than 1 mg L^{-1} after dilution, so they are unlikely to complicate the precursor synthesis. Concentration of Ni and Co can be adjusted by salt addition. Further performance evaluation of an NMC cathode material produced from the purified anode

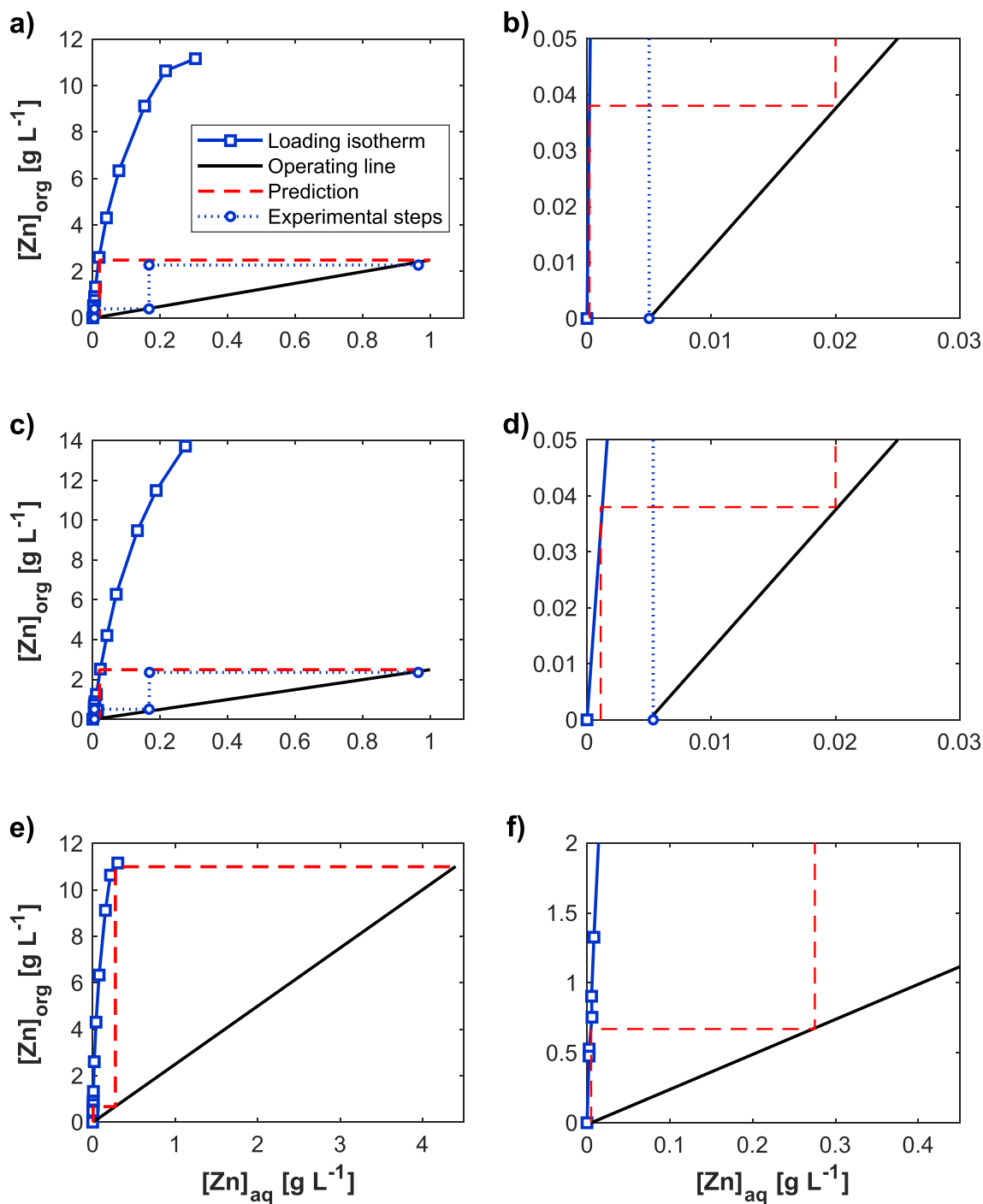


Fig. 8. McCabe–Thiele analysis of the countercurrent extraction of Zn at pH = 3.0 by 0.8 M BTMPPA (a & b) and 0.8 M D2EHPPA (c & d) from the anode sludge leachate in comparison with the experimental results. Subfigures e) and f) show the construction for 0.8 M BTMPPA and an aqueous feed solution with $[Zn]_{0,aq} = 4.4 g L^{-1}$.

sludge leachate (Table 5) involves precursor synthesis, battery manufacturing, and voltammetric testing that have been made but are not in the scope of this paper. Ni, Co, Cu, Zn and Fe are also in the tolerable range for the Mn electrolysis (Lu et al., 2014; Louis et al., 1859). According to our knowledge, no deteriorating effects of Al, Ca, Mg and Na on Mn electrolysis have been reported in the literature. Al, Ca, Mg and Na have lower standard reduction potentials than Mn

(Electrochemical series, 2020), so it is assumed that they are not deposited on the Mn cathodes. Not all impurities were extracted by D2EHPPA or BTMPPA from the anode sludge leachates in this work. Therefore, another approach or additional treatment must be applied if the purity of the $MnSO_4$ solution must be higher than presented in Table 5.

Table 5

Approximate composition of the purified anode sludge leachate (i.e. raffinate from solvent extraction) and concentrations of the diluted raffinate in potential re-use applications.

	Unit	Raffinate from solvent extraction	Electrolytic Mn	NMC622 co-precipitation	NMC811 co-precipitation
Mn	g L ⁻¹	153.1	45	22	11
Na	g L ⁻¹	24	7.1	3.4	1.7
Mg	mg L ⁻¹	208.4	61.3	29.9	15
Al	mg L ⁻¹	80.3	23.6	11.5	5.8
K	mg L ⁻¹	2926.6	860	420	210
Ca	mg L ⁻¹	188.3	55.3	27	13.5
Fe	mg L ⁻¹	1	0.3	0.1	0.1
Co	mg L ⁻¹	4.2	1.2	0.6	0.3
Ni	mg L ⁻¹	2.2	0.6	0.3	0.2
Cu	mg L ⁻¹	4.9	1.4	0.7	0.4
Zn	mg L ⁻¹	3.7	1.1	0.5	0.3

4. Conclusions

Purification of Mn-rich anode sludge leachates by solvent extraction with D2EHPA and BTMPPA was studied. Both extractants can be used to remove Zn and Fe from a concentrated MnSO₄ solution. BTMPPA had higher selectivity for Zn and Fe over Mn than D2EHPA in all studied conditions. Over 99.5 % removal of Zn and Fe was obtained with 0.8 M Na-D2EHPA and 0.8 M Na-BTMPPA in two countercurrent extraction stages operating at S/F = 0.43 under 22 ± 1 °C. The concentration of Zn was decreased from approximately 1000 mg L⁻¹ to below 10 mg L⁻¹. Additionally, the concentration of Fe decreased from 135 mg L⁻¹ to 2 mg L⁻¹ or below. Extraction by 0.8 M Na-BTMPPA lowered Zn and Fe concentrations in the raffinate below 10 mg L⁻¹ only when both countercurrent extraction stages operated at pH = 3. With 0.8 M Na-D2EHPA, concentrations of Zn and Fe in the raffinate were lowered below 10 mg L⁻¹, also when the pH was adjusted to 3 only in the organic feed stage; with the aqueous feed stage operating around pH = 2. Increasing the mean residence time in the mixer from 3.6 min to 6.0 min improved the removal of Zn and Fe with BTMPPA, but with D2EHPA the change in extraction performance was marginal. The mole fraction of Mn in the organic phase ($f_{Mn,org}^*$) decreased with increasing metal loading with both D2EHPA and BTMPPA, so the co-extraction of Mn can be significantly limited by crowding the extractants. $f_{Mn,org}^*$ in crowded BTMPPA solutions was between 9 and 15 mol-% and remained in this range in crowded BTMPPA at all studied pH values. Proton activity has a considerable effect on the crowding characteristics of D2EHPA. The $f_{Mn,org}^*$ in crowded 0.8 M D2EHPA was 65.3 mol-% at pH 1.7 but only 34.9 mol-% at pH 3.7. 55.7 % of the co-extracted Mn was selectively stripped ($P_R(Mn) > 99.5$ wt%) by 0.5 M H₂SO₄ from loaded D2EHPA, whereas 71.5 % of the co-extracted Mn could be stripped from BTMPPA, respectively. Ca and Mg were not significantly extracted by either 0.8 M Na-D2EHPA or 0.8 M Na-BTMPPA at pH = 3. The Zn- and Fe-barren MnSO₄ raffinate contained over 145 g L⁻¹ Mn, around 50–100 mg L⁻¹ Al, 200 mg L⁻¹ Ca and 200 mg L⁻¹ Mg. Precipitation and gelation was encountered in the mixer-settlers in continuous runs when pH increased to 3.0 or above, but solids were not observed in the extract and raffinate outlets or in the batch extraction experiments. The purified MnSO₄ leachate and the Mn-rich fraction of the stripping raffinates are proposed for use in the synthesis of NMC-cathode precursors or for manufacturing electrolytic manganese metal.

CRediT authorship contribution statement

Niklas Jantunen: Methodology, Investigation, Data curation, Formal analysis, Writing – original draft, Visualization. **Toni Kauppinen:** Methodology, Investigation, Data curation, Formal analysis,

Writing – review & editing. **Justin Salminen:** Conceptualization, Resources, Project administration, Writing – review & editing, Supervision, Funding acquisition. **Sami Virolainen:** Conceptualization, Methodology, Validation, Formal analysis, Data curation, Writing – review & editing, Supervision. **Ulla Lassi:** Conceptualization, Resources, Project administration, Writing – review & editing, Supervision, Funding acquisition. **Tuomo Sainio:** Conceptualization, Resources, Project administration, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2021.107200>.

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