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CLEANER MANUFACTURING OF CRITICAL METALS

Recovery of High-Purity MnO₂ from the Acid Leaching Solution of Spent Li-Ion Batteries

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Hydrometallurgical recycling processes for spent Li-ion batteries (LIBs) often produce pregnant leach solutions (PLS) that contain metals like Co, Ni, Mn, Li, Al, etc. Although significant research has focused on the recovery of the most valuable materials (e.g., Co, Ni, Li), the reclamation of Mn from PLS is often neglected. In this study, recovery of Mn via a multi-step process based on solvent extraction with di-2-ethylhexyl phosphoric acid, scrubbing, stripping and oxidative Mn precipitation has been undertaken. The results demonstrate that more than 99% of Mn can be successfully recovered as a high-purity MnO_2 product (purity > 99.5%) with almost no loss of Co, Ni and Li. In addition, the behavior of other metal elements present in the PLS were also studied in detail. Overall, this study investigates the fundamentals of Mn recovery from the complicated PLS of LIBs waste and outlines industrial process feasibility based on known unit process steps.

INTRODUCTION

Li-ion batteries (LIBs) are widely utilized in consumer electronics, energy storage systems and automotive applications due to their high energy density, cell voltage, lack of susceptibility to the memory effect and attractive cycle life. Typically, LIB types based on lithium ion manganese-based oxides that include LiMnO₂ (LMO), LiMn₂O₄, Li₂MnO₃ and lithium nickel manganese cobalt oxides (LiNi_{1-x-v} $Mn_xCo_vO_2$, NMC) are widely used for electric vehicles and medical equipment due to their lower risk of fire or explosion when compared to those based on lithium cobalt oxide $(LiCoO_2)$. Use of NMC in particular is increasing in automotive applications as the main end-users of new battery technology like Tesla, 3M, BMW and GE have shifted toward utilization of $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ battery chemistries. Due to the significant increased use of LIBs in electric vehicles—currently forecast to expand from 21 GWh in 2016 to 1300 GWh by 2030^2 —and their limited lifespan of 5–8 years in vehicle-based applications, large quantities of spent LIBs based upon LMO and NMC will be produced in

the near future.³ Consequently, there will be an increasing demand for the recycling of spent LIBs, in terms of Co, Ni, Li and Mn.

Although there has been a large body of research related to the recycling of LIB wastes by pyrometallurgical and hydrometallurgical methods, a majority have only focused on the recovery of Li, Co, and Ni, whereas Mn retrieval has been less well studied.^{4–7} Moreover, there are currently almost no major recycling technologies available for the recovery of Mn from industrial LIB waste as it is usually composed of both active materials (e.g., NMC) as well as impurities like Al, Fe and Cu.⁸ As a result, battery wastes with these types of compositions are distinctly different from other Mn-bearing resources like Mn oxide minerals,⁹ alkaline Zn-Mn battery waste¹⁰ and deep-sea cores¹¹ when used as a secondary raw material. Consequently, the current technologies used to recover Mn from primary resources are unsuitable for the recovery of Mn from LIB waste, which, in addition to the relatively low price of Mn (e.g., US\$1800–1950 per metric ton for electrolytically produced MnO_2^{12}), further reduces the incentives for improved Mn recovery methodologies.

Nevertheless, Mn is always considered to be a problematic impurity when recycling LIB waste, for example, it has been shown that the presence of Mn in LIB waste affects cobalt alloy production quality and the efficiency of state-of-art smelting technologies.¹³ In addition, research by Granata et al.¹⁴ has revealed that Mn with a concentration of only 3 g/L can significantly reduce the selective separation of cobalt from nickel by the widely utilized solvent, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272). As a result, it is essential to develop a technology to recover or separate Mn from the target Co, Ni, and Li.

In the current study, the possibility to separate or recover valuable metals, and in particular Mn, by hydrometallurgical unit processes is investigated. By a combination of neutralization, solvent extraction (SX) and an oxidative precipitation process, a high-purity MnO_2 product could be produced with almost no loss of other valuable metals like Co, Ni and Li. Simultaneously, impurities like Fe and Al were also removed to produce a solution that contained only Co, Ni, and Li and which is suitable as a feedstock for current Co, Ni, and Li recovery processes.^{15,16}

EXPERIMENTAL

Materials

The original pregnant leach solution (PLS) was produced from industrial waste LIBs according to our previous research,¹⁷ under the conditions of: 2 M H₂SO₄, 2 vol.% H₂O₂, $T = 75^{\circ}$ C, t = 120 min and a solid-to-liquid ratio of 100 g/L. Chemical analysis of the initial acid leaching solution (PLS1) is shown in Table I. Organic solvents for the solvent extraction process like di-2-ethylhexyl phosphoric acid (D2EHPA; 97%, Aldrich) and kerosene (low odor; Alfa Aesar) were used in their as-received form. The other chemicals utilized, like KMnO₄ and NaOH, were all of analytical grade.

Experimental Procedures

Initial Purification of PLS

First, copper recovery from PLS1 was conducted by the addition of iron powder (1.2 times the stoichiometry) at pH 2 and room temperature. The resultant Cu-free solution was then oxidized by the addition of H_2O_2 (1 v/v%, 60°C, 30 min) and neutralized to pH 3.5 (NaOH solution, 5 mol/L), to allow a majority of the Fe and part of the Al to precipitate. After filtration, the resulting solution was utilized in the subsequent Mn recovery process.

Solvent Extraction

The separation of Mn from Co, Ni and Li was carried out by solvent extraction using D2EHPA. Organic and aqueous solutions were mixed in separating funnels and then placed in an incubator shaker (Model KS 3000i; IKA, Germany) with a controlled shaking speed (250 rpm) and temperature (25°C). Batch extraction experiments were performed to optimize extraction conditions in terms of aqueous-to-organic (A/O) phase ratios, equilibrium pH and D2EHPA concentration—in order to obtain the maximum Mn/Co separation factors and minimum loss of Co, Ni and Li. Under the optimum conditions (A/O = 1:2, D2EHPA = 0.4)M, pH 3.2), two series of experiments (Series 1 and Series 2) were conducted to simulate the continuous counter-current extraction process, following the procedures presented by Cheng.¹⁸ In order to simulate the first stages of counter-current extraction, Series 1 were conducted by contacting the same organic consecutively with three new aqueous solution samples (PLS3). Concentrations of metals in that organic sample were analyzed by measuring the stripping solution of organics (10 min, 6 M HCl) with ICP-OES. In contrast, the last stages were simulated by experiments of Series 2, in which, the same aqueous solution (PLS3) was in contact with fresh organics three times.

In order to simulate the industrial scrubbing and stripping process, the loaded organic solvent from Series 1 was initially eluted with MnSO₄ solution in two consecutive steps (A/O = 1:10, t = 5 min, Mn: 4 g/L, pH 4.0), resulting in two separate scrubbing solutions (S1 and S2) and a Mn-rich organic solution (O1). The organic phase (O1) was then subjected to two-step stripping; In the first step, parameters that included H₂SO₄ concentration, stripping time and A/O ratios were investigated in order to achieve complete recovery of the Mn as well as part of the Al present. In the second step (not detailed in this study), the organic solution was further treated by 6 M HCl (A/O = 1:10) in order to remove the residual ions (Fe and Al) and to regenerate the solvent for reuse. The extraction of elements (ϕ) and the separation factors of Mn in preference to other elements $(\beta_{\rm E}^{\rm Mn})$ were calculated as follows:

Table I. Variation in chemical composition and solution pH during the initial purification process

Sample	Element							
	Mn	Со	Ni	Li	Cu	Fe	Al	РН
PLS1 (g/L) PLS2 (g/L)	3.66 3.66	19.33 19.33	$5.19 \\ 5.19$	$\frac{3.58}{3.58}$	$\frac{2.57}{0.02}$	0.52 3 46	$\frac{2.04}{2.04}$	$0.3 \\ 2.0$
PLS3 (g/L)	3.67	19.23	5.17	3.55	0.02	0.48	1.65	$\frac{2.0}{3.5}$

$$\varphi = 100\% \times (C_0 - C_1)/C_0 \tag{1}$$

$$\beta_{\rm E}^{\rm Mn} = (X_{\rm Mn}^{\rm o} X_{\rm E}^{\rm a}) / \left(X_{\rm E}^{\rm o} X_{\rm Mn}^{\rm a} \right) \tag{2}$$

where C_0 and C_1 are the initial and final concentration of the metal in aqueous solution, and X_{Mn}^o, X_E^o and X_{Mn}^a, X_E^a are the mole fractions of Mn and other elements in the organic phase and aqueous solution, respectively.

Mn Recovery by Oxidizing Precipitation

Precipitation of Mn was performed with 0.5 mol/L KMnO₄ and the effect of KMnO₄ dosage was investigated in an agitated solution (500 rpm/min) for a reaction time of 60 min at room temperature. The resultant MnO₂ precipitate was filtered and washed with hot distilled water (ca. 80°C) before being dried at 60°C for 24 h. Filtrates were then subjected to ICP analysis for the calculation of Mn recovery (*E*):

$$E = 100 - 100 \times C_2' V_2' / (C_0' V_0' + C_1' V_1')$$
 (3)

where C'_0, C'_1, C'_2 are the concentrations of Mn in the PLS, KMnO₄ solution, and the filtrate after Mn precipitation, respectively, whereas V'_0, V'_1, V'_2 correspond to the volumes of these solutions.

RESULTS AND DISCUSSION

Initial Purification of the Leaching Solution

The leaching solution (PLS1) was rich in battery metals (Ni, Co, Mn and Li) and impurities like Fe, Al and Cu (shown in Table I). Based upon previous research,¹⁹ Cu was first recovered as high-purity copper powder by cementation, i.e., utilization of redox replacement phenomenon. In this study, copper powders were recovered using 1.3 times the stoichiometric amount of iron powder at pH 2, which gave a recovery of > 99% (supplementary Fig.S-1, in online supplementary materials) and impurities within the copper product of ca. 0.2% (supplementary Fig.S-2). The resultant copper-free solution (PLS2), that contained less than 20 ppm Cu, was then subjected to oxidization $(H_2O_2: 2\% v/v;$ pH \sim 2) and neutralization at pH 3.5 (supplementary Fig.S-3), which resulted in the majority of Fe (ca. 90%), some Al (ca. 20%) and a trace amount of Co (0.5%) being removed. Through these purification steps, the concentrations of the impurity elements in the solution were reduced to 0.02 g/L Cu, 0.48 g/L Fe and 1.65 g/L Al (PLS3). Further details about the initial purification process can be found in the supporting information.

Mn Separation from Other Elements by Solvent Extraction

The commercial solvent, D2EHPA, has been widely used for the purification of Ni and Co sulfate-containing solutions. For example, Cook and Szmokaluk have reported that the Mn concentration in Co-rich raffinate (ca. 10 g/L Co) could be reduced to a level of a few ppm by multistage solvent extraction process with D2EHPA.²⁰ According to the literature, extraction of metals in D2EHPA follows the order: Fe³⁺ > Zn²⁺ \approx Ca²⁺ > Fe²⁺ > Cu²⁺ \approx Mn²⁺ > Co²⁺ \approx Ni²⁺ > Mg²⁺ > Li⁺ based on their pH₅₀ values.^{18,21} From the data, it appears that D2EHPA should provide a good separation of Mn from elements like Co, Ni and Li. Nevertheless, as the pH₅₀ values for metals are usually obtained from ideal single element solutions, use of multi-metal mixtures typical for hydrometallurgical solutions may result in non-ideal behavior.

Batch Extraction Experiments with D2EHPA

Figure 1a, b, and c shows the extraction of Co, Ni, Mn, Al, Fe and Li from PLS3 as a function of equilibrium pH, A/O ratios and D2EHPA concentration. Furthermore, extraction isotherms of Mn, Fe and Al are displayed in Fig. 1d at pH 3.2 (25°C). From the results illustrated in Fig. 1a, b, and c the extraction of metals in D2EHPA is seen to follow the order: $Fe > Al > Mn > Co > Ni \approx Li$, with the extraction of Co, Ni and Li observed to be much lower than that of Fe, Al, and Mn. This suggests that the selective extraction of Fe, Al, and Mn from Co, Ni and Li can be achieved under optimized conditions. For example, extraction of Fe, Al and Mn were in excess of 80%, whereas Co, Ni, and Li extractions remained below 1% at pH 3.2 with A/ O = 1:2 and 0.4 M D2EHPA. Based upon the equilibrium results in Fig. 1c, the extraction isotherms for Fe, Al and Mn were plotted in Fig. 1d. A sharp and linear extraction isotherm for Fe and Al can be observed, indicating that D2EHPA has a very strong extraction ability towards Fe and Al under the investigated conditions. Interestingly, Mn extraction shows an upward trend when the A/O ratio is below 1:1, and then it decreases substantially as the A/O ratio is increased to 2:1. This finding probably results from a lack of reactive sites for complexation and the increase in competitive extraction of Al and Fe as the A/O proportions are increased to 2:1. In the case of the other elements (Co, Ni and Li), their extraction isotherms are not presented as their extractions were of an insufficient level to form an isotherm.

The corresponding separation factors of Mn in relation to the other five elements are listed in supplementary Table S-I. Separation factors of Mn over Co, Ni and Li were determined to be in the hundreds, which indicates a good separation towards Mn. In comparison, the low separation factors of Mn/Fe (< 0.1) highlights that there is a good separation of Fe over Mn. Conversely, the separation factors of Mn over Al are close to 1.0, which suggests a difficult separation between these elements by D2EHPA.



Fig. 1. Extraction of metals as a function of (a) equilibrium pH values (A/O = 1:1, [D2EHPA] = 0.4 M, t = 15 min), (b) D2EHPA concentration (A/O = 1:1, pH 3.2, t = 15 min) and (c) A/O ratios (pH 3.2, [D2EHPA] = 0.4 M, t = 15 min). (d) Is the extraction isotherms of Fe, AI, Mn (pH 3.2, [D2EHPA] = 0.4 M, t = 15 min).

Multiple Stage Extraction

Based upon the above results of batch experiments, a three-stage continuous counter-current extraction process was simulated under the condition of A/O = 1:2, D2EHPA = 0.4 M, pH 3.2, t = 15 min. In order to simulate the change of metal concentration in organic phase during the threestage solvent extraction process, Series 1 was conducted with the same organic sample consecutively contacted by three new PLS3 solutions. The results in Table II show that Fe. Al and Mn were clearly extracted to the organic phase and that their concentration in the organic phase increases with the increased number of extraction stages. Also, Co extraction was evident in the first SX stage (loading up to 281 ppm); however, with further contact with fresh PLS3, Co was crowded back to the PLS. The same phenomenon was also observed with Ni and Li. After three contacts with the PLS3, the organic phases were loaded with 0.57 g/L of Fe, 1.20 g/L of Al, 1.59 g/L Mn and less than 0.02 g/L of Co, Li and

Ni. These findings indicate that the extracted or entrained Co, Ni and Li in the organic phases can be effectively crowded out by Fe, Al and Mn.

In contrast, Series 2 simulated the change of aqueous solution with the same PLS3 sample contacted by new organic samples three times. As observed, the concentration of Fe, Al and Mn decreased to a few ppm after three extraction stages with fresh organic solutions. The Co, Ni and Li concentration remained almost the same after the first two stages of extraction. Nevertheless, at the 3rd stage of contact with fresh organic solvent, approximately 38% of Co and 5% of Ni and Li were co-extracted. The high extraction of Co, Ni, and Li during the 3rd stage extraction can be attributed to the availability of too many complexation sites within the organic solvent and reduced competition from Fe, Al and Mn.

Overall, it can be concluded from the results of Series 1 and 2 that more than 99% of Mn, Al and Fe could be extracted from the aqueous solution by the multistage extraction experiments and that most of

	Concentration of elements (g/L)						
Multiple extraction at pH 3.2	Fe	Al	Mn	Со	Ni	Li	
Organic phase (Series 1)							
0	0.000	0.000	0.000	0.000	0.000	0.000	
1	0.182	0.571	0.998	0.281	0.010	0.048	
2	0.381	0.784	1.535	0.196	0.006	0.029	
3	0.568	1.198	1.594	0.016	0.006	0.018	
Aqueous solution (Series 2)							
0	0.260	1.620	3.320	22.650	4.580	3.367	
1	0.003	0.193	0.580	22.073	4.580	3.357	
2	0.002	0.101	0.024	23.443	4.590	3.385	
3	0.001	0.015	0.003	14.173	4.363	3.221	

Table II. Metal concentration in organic (Series 1) and aqueous solutions (Series 2) during multiple stage extraction at pH 3.2 (A/O = 1:2, t = 15 min)

Table III. Concentration of elements in the two-stage scrubbing solutions (S1 and S2) and the resultant organic solution (O1)

Solution		Concentration of elements (g/L)							
	Fe	Al	Mn	Со	Ni	Li			
S1	< 0.003	0.172	2.581	1.291	0.124	0.230			
S2	< 0.003	0.098	3.721	0.326	0.011	0.041			
01	0.560	1.159	1.551	< 0.003	< 0.003	< 0.003			

the co-extracted Co, Ni, and Li could be crowded out from the loaded organic phases by Mn, Al and Fe.

Stripping Process of Loaded D2EHPA

Scrubbing Process The aim of scrubbing the organic phase is to replace the co-extracted or mechanically entrained Co, Ni or Li together with Mn. The loaded organic from Series 1 was contacted twice by pure $MnSO_4$ solution (Mn: 4 g/L) under the conditions of A/O = 1:10, t = 5 min. The initial pH of the MnSO₄ scrubbing solution was 4 and no further pH adjustment was performed during the scrubbing process. Table III shows the chemical composition of the scrubbing solutions (S1, and S2) and the resultant organic solution (O1). As observed from Table III, after two scrubbing stages, the co-extracted Co, Ni, and Li in the organic solution were almost completely replaced by Mn, resulting in an organic solvent (O1) with almost no Co, Ni, and Li (< 0.003 g/L) and scrubbing solutions (S1 and S2) that contain Mn, Co, Ni and Li. Moreover, the Al concentrations in S1 and S2 were found to be ca. 0.2 g/L and 0.1 g/L, respectively, which suggests that part of the Al (ca. 2.3%) was also substituted by Mn in the organic phase indicating that a scrubbing solution with lower Mn concentration (< 4 g/L) should be used. The scrubbing solution produced could be circulated back into the solvent extraction

process, whereas the resultant organic solution can be subjected to a selective stripping process.

Selective Stripping of Mn Stripping behaviors of Fe, Al, and Mn from the resultant organic phase after scrubbing (O1; Table III) were investigated in terms of H₂SO₄ concentration (0.01–1.0 mol/L), A/O ratio and stripping time. It can be clearly seen from Fig. 2a, that Mn is stripped in preference to Al and Fe over the range of H_2SO_4 concentration investigated and that the following sequence of Mn >Al < Fe (A/O = 1:1, t = 30 min) is established. Complete Mn stripping could be achieved with 0.5 mol/L H₂SO₄, which also results in Al stripping of ca. 40% and Fe stripping of only 0.2%. Nevertheless, with further increases of H_2SO_4 concentration from 0.5 mol/L to 2.0 mol/L the level of Al stripping remains at around 40%, which implies that the other ca. 60% of the extracted Al ions have a higher affinity towards D2EHPA, and that stronger stripping agents like HCl need to be adopted in order to achieve complete Al stripping. In contrast, in the case of Fe, the stripping yields in the acid concentrations investigated remained relatively low at < 3%.

Figure 2b and c illustrates the influence of A/O ratios and stripping time with 0.5 mol/L H_2SO_4 . As observed in Fig. 2b, as the stripping time is extended, Al and Mn show similar behavior and



Fig. 2. Stripping of elements from the loaded organic as a function of (a) H_2SO_4 concentration (A/O = 1:1, t = 30 min), (b) stripping time (A/O = 1:1, [H_2SO_4] = 0.5 M) and (c) A/O ratios ([H_2SO_4] = 0.5 M, t = 10 min). (d) Displays the separation factors of Mn/Al and Al/Fe determined for different concentrations of H_2SO_4 .

both reach equilibrium after 10 min. In Fig. 2c, an increase of the A/O ratios has a limited influence on Mn stripping, which maintains a high level of ca. 98%, whereas Al stripping decreases by nearly 20% from ca. 45% (A/O = 1:1) to 25% (A/O = 1:8). The variation of separation factors with H₂SO₄ concentration is presented in Fig. 2d. The results show that the separation factor of Mn towards Al increases with increasing H_2SO_4 concentration, whilst that of Al towards Fe shows an initial rise in the range of 0.01-0.5 mol/L, before a dramatic decrease is observed at higher acid concentrations. In order to produce a stripping solution that allows a high Mn extraction and low associated impurities, the optimal H_2SO_4 concentration is suggested to be in the region of 0.2-0.5 mol/L. Overall, selective with $H_2SO_4 = 0.5 \text{ mol/L}$, stripping A/O = 1:8,t = 10 min, allows ~ 99% Mn and 25% Al to be stripped, to give a high-Mn-low-impurity solution composed of approximately 12 g/L Mn and 2 g/L Al and almost no other impurity metals (Fe, Ni, Co: < 0.025 g/L, Li: < 0.01 g/L).

Mn Recovery by Oxidative Precipitation

The resultant Mn-rich solution was subjected to oxidative MnO_2 precipitation with $KMnO_4$, as outlined in reaction (4) (T = 298 K).

$$\frac{Mn^{2+} + 2MnO_4^- + 2H_2O = 5MnO_2(s) + 4H^+}{\Delta G = -143.6 \text{ kJ/mol.}}$$
(4)

It can be seen from Fig. 3a that Mn recovery increased with the higher amounts of KMnO₄ and that up to 99% Mn could be recovered with an equal stoichiometric amount of KMnO₄, as would be expected from the Mn oxidization reaction (4). The resultant filtrate contains < 18 ppm Mn and the purity of the MnO₂ product is up to 99.5%; impurity elements like Co, Fe, and Al are all less than 0.02% (Fig. 3b). In contrast, Fig. 3c shows the direct precipitation of Mn from non-purified solution (PLS3) in the presence of other elements, which has been previously reported as a method to recover Mn from LIB leaching solution.²² It can be seen that Mn precipitation recovery from PLS3 is obviously



Fig. 3. Influence of the KMnO₄ consumption on the recovery of Mn and morphology of the MnO₂ product from (a, b) stripping solution and (c, d) PLS3 solution. SEMs of the MnO₂ product include associated impurity values.

lower compared to the purified stripping solution (Fig. 3a) with the same stoichiometric consumption of KMnO₄. From PLS3, the maximum Mn precipitation achieved is only ca. 80% when 1.5 times the stoichiometric amount of KMnO₄ was consumed. Moreover, cobalt precipitation is also observed to increase with higher levels of KMnO₄ additions, and with cobalt precipitation levels of > 8% with 1.5 times the stoichiometry of KMnO₄ this results in impure MnO₂ products with $\sim 9\%$ Co and 0.7% Fe (Fig. 3d). Furthermore, a more detailed examination of the SEM images (Fig. 3b and d) shows that there are distinct morphological differences between the MnO₂ products formed depending on the solution. For example, the MnO_2 produced from the purified stripping solution has a more uniform particle size (< $2 \mu m$) than that produced from PLS3, which has a much more inhomogeneous appearance as a result of the relatively high level of impurities like Co.

Figure 4 displays the Eh-pH diagram of the Mn-Co-H₂O system for 0.05 M Mn and 0.35 M Co at 25°C (HSC 9.2.6; Outotec Technologies). The upper left green region is the overlapping domain of soluble Co (II) and Mn precipitate below the O_2 formation line (upper dashed line), in which the



Fig. 4. Eh-pH diagram of Mn-Co-H₂O for 0.05 M Mn and 0.35 M Co at 25°C.

thermodynamics predict selective precipitation of Mn without the co-precipitation of Co. Such a narrow operating range of Eh and pH values suggests the difficulty in obtaining high-purity MnO_2 in the presence of Co ions, which are prone to be oxidized as a Co_3O_4 precipitate via reaction (5) (298 K):



$$9 \text{Co}^{2+} + 2 \text{MnO}_4^- + 8 \text{H}_2 \text{O} = 2 \text{MnO}_2(s) + 3 \text{Co}_3 \text{O}_4$$

+ $16 \text{H}^+ \quad \Delta G = -29.3 \text{ kJ/mol}$

 $(\mathbf{5})$

In principle, a high-purity MnO_2 product can be produced from the acid leaching solution of LIB waste by a combination of solvent extraction with D2EHPA, selective stripping and oxidative precipitation, as presented in Fig. 5. Note that this study does not include details of the recovery of Co, Ni, and Li, which can be achieved by state-of-art SX-EW (solvent extraction and electrowinning) processes, followed by Li recovery from the raffinate as Li_3PO_4 or Li_2CO_3 .^{4,23} One advantage of the current approach is that, after partial neutralization of the Fe and Al, the rest of these impurities can be coremoved from the PLS along with Mn removal, already at a low pH (pH ~ 3.2), and thus the coprecipitate can be avoided.²⁴ The Mn recovery methodology proposed has excellent potential, as the technology required for the different unit processes is readily available and in use on an industrial scale for other applications.

CONCLUSION

Manganese present in LIB waste has always been treated as an impurity element and its recovery has often been overlooked due to the low price of Mn, in comparison with valuable battery metals like Co, Ni, etc. Nevertheless, due to the rapid growth in the electric vehicle sector and pressure on finite material resources, the recycling of all battery materials is becoming increasingly significant in the circular economy of metals. The current study addresses the issue of Mn recovery by: acid leaching-Cu cementation-neutralization, followed by Mn solvent extraction with D2EHPA, scrubbing with MnSO₄ solution, selective stripping and oxidative precipitation with $KMnO_4$. MnO_2 with a purity of above 99.5% is produced by the presented approach. The developed process has a significant potential for large-scale applications since all the utilized methods are based on known unit processes. Nevertheless, the resultant waste solution after Mn precipitation contains relatively high levels of K and Al, which may cause challenges in the solution circulation between process steps. This can be potentially overcome by the removal of Al through neutralization, and a subsequent recovery of the impure K_2SO_4 product by evaporation, to be utilized, e.g., as fertilizer.

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ELECTRONIC SUPPLEMENTARY MATERIAL

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