Recovery and application of magnetic nanosized sorbents from lithium-ion recycling secondary streams.

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9 Abstract

10 The secondary pollution from hydrometallurgical recycling of lithium ion batteries (LIBs) is a

11 concern affecting the process sustainability. This study explores the reuse of two LIB processing

12 streams (iron-sludge and Mn-stripping effluent) to produce magnetic nanosized sorbents.

13 A surfactant-autoclave synthesis was carried out to obtain CuFe₂O₄ (15 nm) from synthetic

14 precursors, and $Cu_{(0.48)}Co_{(0.40)}Mn_{(0.10)}Ni_{(0.02)}Fe_2O_4$ (12 nm) from iron-sludge. Both products exhibited

15 crystallite size less than 20 nm and a narrow size distribution. These materials were used for sorption

tests on synthetic solutions and pretreated Mn-stripping effluent. Mn preferential sorption ($\approx 16 \text{ mg/g}$)

17 versus Co, Li and Na was noticed. Mn and Co removal from pretreated effluent increased using the

recycled material (Mn 100%, Co 70%) rather than $CuFe_2O_4$ (Mn 91%, Co 59%).

Furthermore, single-phase nanocrystalline $Mn_{(0.63)}Co_{(0.35)}Ni_{(0.02)}Fe_2O_4$ ferrites were entirely resynthesized from the two LIB streams by an ultrasound-surfactant-microwave treatment. A broader crystallite size distribution was achieved, compared to autoclave materials. When dried at 100 °C sizes ranged up to 57 nm, while sintering at 700 °C to 98 nm.

Distinct physical- and chemical properties (i.e. magnetization, porosity, sizes) were studied to assess
either the effect of the advanced hydrothermal routes and of the starting materials on the final
products.

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27 Keywords: lithium-ion battery recycling, secondary streams valorisation, nanosized ferrite,

28 hydrothermal synthesis, magnetic sorbents

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30 1. Introduction

The widespread application of lithium ion battery (LIB) in electronic devices and in electric vehicles (EVs) has newly remarked the technological and societal challenges for LIB recycling [1]. According to the circular economy, the lack of appropriate recycling technologies may seriously affect the sustainability of EV life-cycle [2].

The large-scale recycling of LIB is often performed by combinations of pyro- and hydrometallurgical processes, whereas higher recovery rates (e.g. lithium, graphite) and sustainability could be achieved by combining physical-chemical pre-treatment with hydrometallurgy [3]. Yet, several aspects hinder the adoption of recycling technologies based on hydrometallurgy. Among them, the difficult upstream battery sorting, the complex scale-up, and environmental issues related to the secondary streams and by-products management (*e.g.* contaminated effluents) [1].

Indeed, even by using state-of-the-art hydrometallurgical technologies the high-grade recovery of graphite, cobalt, nickel, and lithium lead to the generation of secondary waste streams (effluents/sludges)[3]. Clearly, a higher sustainability would be achieved if these secondary streams were reused instead of being disposed.

45 A profitable way to reuse such secondary streams wastes might rely on the production of mixed iron oxides, such as ferrites. Ferrites are a class of compounds, including iron oxides having a spinel-like 46 structure, e.g. magnetite Fe₃O₄, where divalent and trivalent iron atoms can be substituted by other 47 metal elements (e.g. Mn, Co, Zn, Mg, etc), to obtain materials with fine-tuned properties of general 48 formula $(M^{2+}_{1-x})(M^{3+}_{x})[M^{2+}_{x}(M^{3+}_{2-x})]O_{4}[4]$. This class of materials finds daily application in gas 49 50 sensing [5], catalysis [6], biomedicine [7], analytics [8], magnetic shielding [9], switching and highfrequencies devices [10,11], electronic devices [4], and as electrode materials for batteries and 51 supercapacitors [12]. 52

For instance, Chen et al. used an electroplating sludge (and a spent pickle liquor) in the presence of
ferric ions to immobilize heavy metals in ferrite materials [13,14], while Erdem and Tumen removed
chromium from solution in ferrite form [15].

The principle of 'Cradle-to-Cradle'', fundamental concept for circular-economy, would be
encouraged forth if the ferrite product obtained from waste had an intrinsic added value (i.e. marketgrade nanopowder) or a ''second-life'' application.

Iron oxides exhibit remarkable sorption features for dissolved metal ions, and spinel ferrite chemical stability in an extended pH range of aqueous solutions [16,17], promote ferrite compounds as suitable sorbent materials [18,19]. These compounds may be positively or negatively charged according to the relative zero point charge (PZC) and pH of the media. Generally, sorption/desorption mechanisms of ionic pollutants *i.e.* heavy metals, onto iron oxides are pH-related and can be reversibly controlled by pH variations due to amphoteric properties of hydroxylic sites [20].

Furthermore, magnetic fields can be exploited to facilitate the downstream separations of sorbents and sorbates from purified liquid streams *e.g.* magnetic field decantation, with benefits to process cost. Evidently, adopting the recycled magnetic sorbent for the purification of LIB recycling wastewaters would present a significant added value to the overall recycling process.

69 The scope of the present work is to investigate the reuse of real secondary streams from the 70 hydrometallurgical recycling of LIBs [21] to produce magnetic nanoferrites to be applied as sorbent 71 material for dissolved heavy metals (Co, Mn).

In our research group, for the first time, ferrite compounds were recovered from LIB recycling byproducts, using secondary streams from LIB hydrometallurgical recycling [21]. This study, in particular, gives an overview on how the combinations of the advanced synthetic techniques (*i.e.* ultrasounds [22], microwaves [23], capping agents) and starting materials, influenced the properties of the ferrite compounds.

While the second part of the work concerns the preliminary sorption tests performed with recycledferrites for cobalt and manganese sorption on real LIB recycling effluent.

79 **2. Experimental**

80 2.1 Materials

For the synthesis of ferrite, reagent-grade CuSO₄ (extra pure, anhydrous, Carlo Erba reagents) and 81 82 $Fe_2(SO_4)_3$ 5H₂O (97%, Sigma-Aldrich) were used as metallic precursors, DTAB (Dodecyiltrimethylammonium bromide- 99%, ACROS organics) as surfactant/capping agent, NaOH 83 (>98%, Sigma-Aldrich) as precipitating agent, and hexane (99%, Sigma-Aldrich) used for washing. 84 CoSO₄·7H₂O (\geq 99%, Sigma-Aldrich), MnSO₄·H₂O (\geq 96%, Riedel-de Haën), Li₂SO₄ (\geq 98%, 85 86 Sigma-Aldrich) and Na₂SO₄ (\geq 99%, Sigma-Aldrich) used to prepare the synthetic wastewater and 87 the H_2SO_4 (96%, Sigma-Aldrich) used to dissolve the iron contained in the solid waste. 88 Two waste streams generated in the recycling process for LiB, described elsewhere [21], were used as starting materials for the synthesis of the nanoferrites, namely the Fe-sludge and the Mn-stripping 89 effluent. The Mn-stripping solution was also used as wastewater to test the adsorption capacity of 90

91 $Cu_{(0.48)}Co_{(0.40)}Mn_{(0.10)}Ni_{(0.02)}Fe_2O_4$ and $CuFe_2O_4$.

92 2.2 Wastes from lithium ion battery (LIB) recycling process

Errore. L'origine riferimento non è stata trovata. shows the schematic flowsheet of an advanced 93 94 LIB recycling process, according to the latest developments presented in a recent publication [21]. 95 The process configuration includes a first stage of tailor-made pre-treatments, followed by a flexible hydrometallurgical section. The hydrometallurgical section, including acid leaching and sequential 96 97 physical- and chemical operations, enables the recovery of high-grade graphite, cobalt, nickel, and lithium products. Briefly, graphite is recovered after 2-stage sulfuric acid leaching, while the 98 emerging leachates are purified from Mn, Al and Cu by 2- step D2EHPA solvent extraction, leaving 99 100 in the resulting solution Co, Ni and Li. Thus, Co is selectively extracted by Cyanex from Ni and Li and can be recovered in different chemical forms after stripping and precipitation. Subsequently, Ni 101 can be precipitated as hydroxide, whereas remaining Li and Na in solutions are recovered as carbonate 102 103 and sulphate form, respectively, upon physical (evaporation-cooling) and chemical (carbonation) operations. 104

Despite the effort undertaken, this method results in the generation of secondary streams. These
secondary streams correspond mainly to the "Fe-sludge" and "Mn-stripping solution".
Both streams contain valuable metals (*i.e.* Fe, Mn, Co) that can be used to produce magnetic sorbents,
a smart alternative to disposal and/or wastewater treatment.





$\begin{array}{c} 110 \\ 111 \end{array}$

Figure 1: LIB recycling flowsheet integrated with ferrite sorbent production

112 **2.2.1 Fe-sludge**

This sludge is generated within the first purification of the leach pregnant solution to precipitate 113 metallic impurities and adjust the pH for solvent extraction at pH 3.8, using NaOH. The Fe-sludge 114 was dried to constant weight at 50 °C prior to characterization and further use. A weighted amount 115 was entirely solubilized in aqua regia (S/L=1:20) using Milestone ETHOS 900 microwave digester at 116 200°C for 30 mins. The resulting solution was analysed by high-resolution continuum source atomic 117 absorption spectrometry (HR-CS AAS, ContrAA 300-Analytik Jena AG) for the analysis of metal 118 concentration. The dry solid was used as iron source for the synthesis of both RCuF and RMnF 119 ferrites. 120

121 **2.2.2 Mn-stripping effluent**

The Mn-stripping effluent is produced within the liquid-liquid extraction section of LIB process, as 122 result of leachate purification by D2EHPA in kerosene. This organic phase selectively separates Mn, 123 Cu, Al from Co, Ni, Li bore in the leachate, in order to recover target products of satisfactory purity 124 125 (graphite, Co, Ni, Li). The metal cations loaded in organic phase are reversibly released into aqueous solution, using H₂SO₄ solutions for cation exchange, producing an acidic sulphate effluent containing 126 Mn. Cu. Al. and minor Co. 127 This acidic solution (pH 0.7) acted as metal source for the synthesis of RMnF powders, as well as a 128 real wastewater to be decontaminated from Mn and Co. To simulate metals precipitation (or Mn/Co 129 recovery attempts) on the Mn-stripping solution, the pH was increased to 8, 9, and 10. After solid-130 liquid separation by vacuum filtration, the three outcoming solutions were used for testing SCuF 131 sorption capability. RCuF powder was only tested after precipitation at pH 8. 132

133 The concentrations of metals in the liquid stream were determined by HR-CS AAS analysis.

134 **2.3 Synthesis of ferrites**

The nanoferrites were prepared using different starting materials and synthetic procedures, given by the distinct combination of advanced hydrothermal treatments (*e.g.* autoclave, microwaves, ultrasounds), dissolution techniques (*e.g.* H_2SO_4 , ultrasounds) and final heat treatments (*e.g.* time, temperature), according to the 5 synthetic routes summarized in Table 1.

Sample	SCuF	RCuF	RMnF HT	RMnF 100	RMnF 700
Precursors	$-Fe_2(SO_4)_3$	-Fe-sludge	-Fe-sludge	-Fe-sludge	-Fe-sludge
	-CuSO ₄	-CuSO ₄	-Mn-stripping	-Mn-stripping	-Mn-stripping
Dissolution	75-min mixing	H_2SO_4	75 min. mixing	30 min. mixing	30 min. mixing
method		75 min. mixing		+	+
				5 min.	5 min.
				sonication	sonication
DTAB	0.1	0.1	0.1	0.03	0.03
$(mol \cdot l^{-1})$					
Precipitation	12.5	12.5	12.5	12.5	12.5
pН					
Post-	75-min	75-min	75-min	30-min.	30-min
precipitation					+ 5-min

139Table 1: Experimental conditions and combinations of treatments used to produce nanostructured powders from synthetic and waste140precursors

mixing				+5-min	sonication
				sonication	
Hydrothermal	Autoclave	Autoclave	Autoclave	Microwave	Microwave
treatment	120°C-1h	120°C-1h	120°C-1h	200°C-1h	200°C-1h
Drying/	100°C	100°C	100°C	100°C	700°C
Sintering	12h	12h	12h	12h	3h

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142 **2.3.1 Synthetic Copper Ferrites (SCuF)**

The SCuF were prepared using the experimental conditions described in a previous work [24], namely precipitation at pH 12.5 in the presence of DTAB, followed by autoclave treatment at 120°C for 1 h. Unlike in [24], after NaOH precipitation, the mixing time was prolonged up to 75 mins. The precipitation slurry was washed three times with distilled water (until final volume of 50 ml) and finally with hexane (10 ml) prior to product recovery and drying at 100°C. The solid-liquid separation during washing was performed by centrifuging the slurries for 5 mins at 3000 rpm.

149 **2.3.2 Mixed copper ferrite from real Fe-sludge (RCuF)**

- The Fe-sludge was preliminary dissolved using a H2SO4 solution (proportions: 1g of iron sludge, 8ml of DI water, 2 ml of 96% H₂SO₄). DTAB was added to the resulting solution to achieve a starting concentration of 0.1 M. Subsequently, 0.14 g of CuSO₄ anhydrous were added up to have [Fe³⁺]/[Cu²⁺] equal to 2, although the total concentration of divalent metal ions is two-fold the theoretical ratio, given by $[Fe^{3+}]/[M^{2+}] = 2$.
- 155 After these operations, the metallic precursors were precipitated with 5M NaOH followed by the 156 hydrothermal synthetic procedure and recovery as for SCuF preparation.

157 2.3.3 Mixed manganese-cobalt ferrite using Fe-sludge and Mn-stripping effluent (RMnF)

- 158 The iron solid waste and Mn-stripping solution were used as straight metal sources for RMnF.
- 159 The acidic Mn-stripping solution was used to dissolve the Fe-sludge. About 0.3 g of dried Fe-sludge
- 160 were dissolved using 10 ml of Mn-stripping solution.
- 161 To produce RMnF via hydrothermal method (RMnF HT), prior to the precipitation stage, the
- dissolution of Fe sludge by Mn-stripping effluent was performed by stirring for 75 mins (600 rpm)
- until complete dissolution. Then, the desired amount of DTAB, to have 0.1 M concentration, was

added and the precipitation took place. After supplementary 30-min mixing the slurry was placed in
autoclave reactor at 120 °C for 1 h.

In contrast, to obtain RMnF *via* microwave assisted hydrothermal method, the Fe sludge was solubilized with Mn-stripping solution, by 30-min mixing (600 rpm) followed by 5-min sonication in laboratory ultrasound bath (ELMA). At this point, DTAB to have 0.03M concentration is added and the precipitation performed. After 30-min mixing (600 rpm)+ 5-min sonication, the mixture was transferred to Teflon-line vessel for the microwave treatment at 500W, 200°C for 1 h- after 5 minutes ramping to the set temperature.

For RMnFHT and 100, the solid-liquid separation, washing, recovery were carried out as for SCuF
and RCuF. However, for RMnF 700 the final sintering was at performed at 700°C for 3h under air.

2.4 Characterization of ferrite products

The chemical and physical characterization of ferrite powders was performed by high resolution field 175 emission scanning electron microscopy using a HR-FESEM (Zeiss Auriga) equipped with EDX probe 176 177 (Bruker). The phase composition of the ferrites products was determined by x-ray diffraction using a XRD (Rigaku D-max) operating at 40 kV and 40 mA, with Cu Ka radiation. Match! v. 2 software 178 was used for phase identification and quantification. Crystallite size was calculated from Sherrer's 179 180 equation, after FWHM (full width half of the maximum) determination from XRD patterns with Origin pro v. 9 software. The specific surface area of the reaction products was determined using a 181 high efficiency specific surface area and pore distribution analyser (ASAP 2010, Shimadzu, Japan) 182 based on the nitrogen adsorption BET method upon driving at 200 °C for 6 h. The magnetic properties 183 of the samples were measured using a physical properties measurement system (PPMS Quantum 184 Design, USA) magnetometer operated at 298 °K from -70 kOe to 70 kOe field. The chemical 185 composition of the obtained products was determined by aqua regia microwave digestion at 220°C 186 for 1 h, 500W prior to HR-CS AAS analysis of the leachates . 187

188 **2.5 Sorption tests**

- All sorption tests were performed at constant sorbent-to-volume ratio (2 g/L), time (24h), temperature (25 °C) and mixing speed (500 rpm). The metal-bearing solutions used in the sorption tests were the synthetic solutions (described below) and the pretreated Mn-stripping effluent solutions.
- 192 The adsorption properties of SCuF were tested on single metal systems (Mn and Co), binary systems
- 193 (Mn+Li; Mn+Na and Co+Li; Co+Na) and quaternary systems (all= Mn+Co+Li+Na) at fixed
- 194 concentrations of Mn (30 mg/L), Co (5 mg/L), Li (30 mg/L), Na (25 g/L) at pH 7.
- 195 The SCuF was tested as sorbent for pretreated Mn-stripping solutions at the three pH levels, whereas
- the RCuF was tested only at pH 9. The pH of Mn-stripping stream was adjusted to 8, 9, 10 through
- 197 the addition of 5M NaOH, mimicking a metal recovery as hydroxides. The solid-liquid separation
- 198 was performed *via* magnetic decantation. The residual metal concentration in solution was determined
- 199 by HR-CS AAS.

200 **3. Results and discussion**

201 **3.1** Characterization of "LIB process" secondary streams

- Table 2 lists the concentration of metals in the iron-sludge and the Mn-stripping solution. The Fe-
- sludge is an amorphous precipitate, showing iron as its predominant metal (10.0%), followed by Co
- 204 (4.2%), Al (2.5%), Ni (0.9%), Cu (0.5%), Mn (0.6%) Li, (0.6%). The Mn-stripping contains Mn
- 205 (1770 mg/L), Al (400 mg/L), Co (340 mg/L), Cu (340 mg/L), Li (66 mg/L) and Ni (14 mg/L).
- Table 2: Characterization of metal content in the waste streams produced within the LIB recycling process and reused for ferrite
 production

Secondary streams	Al	Со	Cu	Fe	Li	Mn	Ni
Fe-sludge (% wt.)	2.5 ± 0.7	4.2 ± 0.3	0.53 ± 0.05	10.0 ± 0.6	0.6 ± 0.2	0.6 ± 0.2	0.9 ± 0.7
Mn-stripping (mg/L)	400 ± 15	340 ± 30	340 ± 20	<lod< th=""><th>66 ± 3</th><th>1770 ± 50</th><th>14 ± 2</th></lod<>	66 ± 3	1770 ± 50	14 ± 2

3.2 Chemical and mineralogical characterization of ferrite products

209 Despite the different starting materials, the SCuF and RCuF obtained after autoclave treatments 210 exhibited similar features (*i.e.* morphology and narrow crystallite size distribution). The XRD patterns

211 (

Figure 2 a) showed for both samples the formation of a main ferrite phase and tenorite (CuO) as secondary phase. This was observed in literature as a prerogative of relatively low temperature of processing/sintering of CuFe₂O₄ [22,24,25].

Quantitative information about phase compositions of the obtained products were obtained through the chemical characterization. For SCuF, the chemical characterization highlighted a molar excess of copper to Fe of about 10% taking as reference the stoichiometry of CuFe₂O₄. This well approximates the formation of a secondary CuO phase accounting for 12% wt. In contrast, the relative amount of tenorite in RCuF was found to be 6% wt.

The lower concentration of CuO in the solid product can be associated with the presence of other cations (Co, Mn, and Ni contained in the Fe-sludge) competing with copper for site occupancy in the ferrite lattice. Likely, smaller lattice units of Co-O (cubic, a = 4.26 Å), Ni-O (cubic, a = 4.17 Å), Mn-O (octahedral, a = 4.43 Å) compared with CuO (monoclinic, a = 4.68 Å, b = 3.42 Å, c = 5.13 Å) may result preferably inserted in the ferrite structure.

225 Considering the relative amount of CuO, the average stoichiometry of the remaining ferrite phase of 226 RCuF was approximated as $Cu_{(0.48)}Co_{(0.40)}Mn_{(0.10)}Ni_{(0.02)}Fe_2O_4$. Unlike these metals included in the 227 ferrrite, Al remained in solution according to its amphoteric behaviour at coprecipitation pH.

The SEM micrographs of SCuF and RCuF ferrites (Errore. L'origine riferimento non è stata 228 trovata. a, b) denoted small crystallites (< 20 nm) with scarce crystallinity and irregular morphology. 229 The particle size of the larger crystallites determined through the SEM profile width approximated 230 19 nm for SCuF and 12 nm RCuF (Table 4). These values were close to the average crystallite sizes 231 determined from the Scherrer's equation, corresponding to 14.5 nm and 11.8 nm, respectively. The 232 agreement between these values support a narrow size dispersion of crystallites for SCuF and RCuF 233 samples, as well absence of pronounced secondary crystallization and nucleation, as denoted by SEM 234 imaging. 235



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Figure 2: XRD patterns of SCuF and RCuF (a) and of RMnF synthesized in autoclave (RMnF HT) and in microwave followed by 100
 °C (RMnF 100) and 700°C (RMnF 700) sintering (b).

	241	Table 3: Metal	l composition	of the	obtained	ferrite	products
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Sample	Al (wt. %)	Co (wt. %)	Cu (wt. %)	Fe (wt. %)	Li (wt. %)	Mn (wt. %)	Ni (wt. %)
SCuF	*N.A.	*N.A.	31 ± 1	49 ± 1	*N.A.	*N.A.	*N.A.
RCuF	<lod< th=""><th>11 ± 1</th><th>15 ± 1</th><th>51 ± 2</th><th><lod< th=""><th>2.5 ± 0.4</th><th>0.3 ± 0.1</th></lod<></th></lod<>	11 ± 1	15 ± 1	51 ± 2	<lod< th=""><th>2.5 ± 0.4</th><th>0.3 ± 0.1</th></lod<>	2.5 ± 0.4	0.3 ± 0.1
RMnF	<lod< th=""><th>9 ± 1</th><th><lod< th=""><th>48 ± 1</th><th><lod< th=""><th>15 ± 2</th><th>0.2 ± 0.1</th></lod<></th></lod<></th></lod<>	9 ± 1	<lod< th=""><th>48 ± 1</th><th><lod< th=""><th>15 ± 2</th><th>0.2 ± 0.1</th></lod<></th></lod<>	48 ± 1	<lod< th=""><th>15 ± 2</th><th>0.2 ± 0.1</th></lod<>	15 ± 2	0.2 ± 0.1
*N.A.= not analysed							

242Table 4: Average formula (from MW digestion and HR-CS AAS analyses of leachates), crystallite size (from Scherrer's equation: $D = 0.9\lambda/\beta \cos\theta$, using gaussian approximation $\beta = FWHM$ on main pure line, *on secondary pure lines and ** profile width243 $0.9\lambda/\beta \cos\theta$, using gaussian approximation $\beta = FWHM$ on main pure line, *on secondary pure lines and ** profile width244measurements of bigger clusters, SEM), d-spacing (from Bragg's law: $n\lambda = 2d \sin\theta$, XRD), lattice constant (from cubic lattice

245	equation: $a=D_{hkl}(h^2+k^2+l^2)^{1/2}$ where $h=k=l$, XRD).
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Sample	Average formula	Crystallite size (nm)		Lattice constant (Å)	d-spacing (Å)
SCuF	CuFe ₂ O ₄ - secondary phase of CuO (12%)	14.5*	**19	8.348	0.252
RCuF	$Cu_{(0.48)}Co_{(0.40)}Mn_{(0.10)}Ni_{(0.02)}Fe_2O_4$ - secondary phase of CuO (6%)	11.8*	**12	8.330	0.251
RMnF100	$Mn_{(0.63)}Co_{(0.35)}Ni_{(0.02)}Fe_{2}O_{4}$	21.9	**57	8.428	0.254
RMnF700	$Mn_{(0.63)}Co_{(0.35)}Ni_{(0.02)}Fe_2O_4$	25.4	**98	8.411	0.252

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The autoclave synthesis was then attempted to reuse simultaneously Fe-sludge and Mn-stripping effluent. Prior to autoclave, Fe-sludge was dissolved with Mn-Stripping solution, however the final product, RMnF HT, obtained from the combination of treatments of Table 1, was a macroscopic amorphous phase of ferrite, as evidenced by XRD (

Figure 2 b) and SEM image (Fig. S1), without any relevant feature at nanoscale. To overcome the

long dissolution time and unsatisfactory morphology, enhanced ultrasounds mixing and microwave

assisted hydrothermal treatments were investigated.

The products obtained after such combination of treatments resulted in ordered nanostructured singlephase ferrites, without any secondary oxide phases, neither after drying at 100 °C nor by sintering at 700 °C.

The RMnF 100 and RMnF 700 showed identical elemental composition, approximating an average stoichiometry corresponding to $Mn_{(0.63)}Co_{(0.35)}Ni_{(0.02)}Fe_2O_4$ for both samples. The sample dried at 100°C (RMnF 100) exhibited cubic-like crystals (**Errore. L'origine riferimento non è stata trovata.** c), while the one sintered at 700°C (RMnF700), showed a partial morphological rearrangement to rhombohedral-like structures (**Errore. L'origine riferimento non è stata trovata.** d).

The SEM micrographs highlighted also for both samples a wider size distribution compared to the Cu-based ferrites. This finding was supported by a consistent discrepancy between SEM and XRD crystallite size estimation. The SEM profile width gave 57 and 98 nm- as most linear extensions, while the average crystallite sizes determined from the Scherrer's equation were 21.9 and 25.4 nm, for RMnF100 and RMnF700, respectively.

Sintering at 700°C produced also a decrease of the lattice parameter and d-spacing from 8.428 to
8.411 Å, and from 0.252 to 0.251 Å, respectively. The more pronounced atom packaging
associated with the sintering at higher temperature (700°C, 3h) is a well-known behaviour for
metallurgical powders and nanocrystalline ceramics [26,27]. The obtained lattice parameters laid
between reference values of pure MnFe₂O₄ (8.499 Å) and pure CoFe₂O₄ (8.391 Å) [28].



Figure 3: SEM micrographs of SCuF (a), RCuF (b), RMnF 100 (c), and RMnF 700 (d).

3.3 BET and magnetic characterization of ferrite products

The nitrogen adsorption/desorption study for SCuF, RCuF, RMnF 100 and RMnF 700 (Figure 4 a-d) indicated a type IV isotherm for all four samples, assimilable to H4 loops [29] and mesoporous materials [30].

Both Cu-based (SCuF and RCuF) and Mn-based (RMnF 100 and 700) ferrites satisfied the nanomaterial classification criterion of volume-specific surface area, VSSA (VSSA= SSA x $\rho > 60$ m² cm⁻³)[31], considering the specific surface areas (**Errore. L'origine riferimento non è stata trovata.**) calculated from BET method and the density of the ferrite materials (\geq 5 g cm⁻³).

In general, the specific surface area was inversely proportional to the crystallite size (Table 5). The small irregular crystallites of Cu-based ferrite from the autoclave treatment exhibited higher BET surfaces (160.7 m^2g^{-1} for SCuF; 168.8 m^2g^{-1} for RCuF) than the Mn-ferrites from the microwave. This behaviour was also observed within the same class of ferrite, where the surface extension for RMnF

288 700 was lower than RMnF 100 (143.7 m²g⁻¹ for RMnF 100 \leq 57 nm; 104.4 m²g⁻¹ for RMnF 700 \leq 98 nm).

The nanoferrites obtained upon autoclave treatment exhibited also a higher porosity than the ones 290 treated with microwaves (Table 5). The cumulative pore volume was found to be 0.22 and 0.23 cm³g⁻ 291 ¹ for SCuF and RCuF against the 0.19 cm³g⁻¹ 0.18 cm³g⁻¹ observed for RMnF100 and RMnF700. 292 Similarly, the average pore diameter for SCuF and RCuF was 8.6 and 8.9 nm, respectively, whereas 293 the ones of RMnF100 and RMnF700 were 7.3 and 6.9 nm. Clearly, the nanoferrite obtained upon 294 microwave treatment at 700°C was associated with the lowest porosity. This evidence can be 295 296 considered as a consequence of the more compact crystal structure, as denoted by the XRD lattice 297 parameters. In other words, the higher temperature resulted in closer atoms and, in turn, a less porous structure. 298

The magnetization *vs* applied field graphs for the four materials are presented in Figure 5. For SCuF (Figure 5 a), RCuF (Figure 5 b), and RMnF 100 (Figure 5 c), the measured magnetizations were 31.7, 26.7 and 27.1 emu g⁻¹ respectively. This values along with the low coercivity (Hc) and residual magnetization (Mr) features are in agreement with literature data for nanosized ferrite compounds, and typical of soft ferrites (**Errore. L'origine riferimento non è stata trovata.**)[32–35].

The lowest coercivity amongst the investigated samples was observed in the RMnF100 (5.2 Oe), whereas the highest saturation to magnetization (Ms) and residual magnetization (Mr) were measured from the RMnF700 (Figure 5 d). The higher Ms can be mainly attributed to the larger crystallites [35,36], although crystallinity, crystal domain, relative chemical composition, grade of inversion, and cation distribution [37], are also known as paramenters influencing the magnetic properties of

- nanosized ferrites [32]. The higher susceptibility to magnetization of this material could be later
 exploited to achieve a better downstream separation (i.e. magnetic decantation).
- 311 Only minor effect of chemical composition on magnetic behaviour was observed in the case of SCuF
- and RCuF.
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Figure 4: N₂ adsorption/desorption isotherms of RCuF (a), SCuF (b), RMnF 100 (c) and RMnF 700 (d)

³²⁰ *obtained ferrite products.*

Sample	Specific surface Area (m ² g ⁻¹)	Cumulative pore volume (cm ³ g ⁻¹)	Average pore diameter (<i>nm</i>)
SCuF	160.7	0.22	8.6
RCuF	168.8	0.23	8.9
RMnF100	143.7	0.19	7.3
RMnF700	104.4	0.18	6.9

³¹⁸ Table 5: Specific surface area $(1/V_{ads}(1/P-1) \text{ vs } 1/P \text{ plot})$, cumulative pore volume (single point total pore volume) and average pore diameter (4V/A, assuming cylindrical pore geometry), saturation to magnetization, residual magnetization and coercive field of the



326 Figure 5: Magnetization vs applied magnetic field plots for SCuF (a), RCuF (b), RMnF100 (c) and RMnF700 (d) with near-zero 327 magnetization insets to appreciate the hysteresis loop.

328 Table 6: Saturation to magnetization (Ms), residual magnetization (Mr) and coercive field (Hc) of the obtained ferrite products.

Sample	Saturation magnetization Ms (emu g ⁻¹)	Residual magnetization Mr (emu g ⁻¹)	Coercive field Hc (Oe)
SCuF	31.7	0.9	24.8
RCuF	26.7	0.8	19.7
RMnF 100	27.1	1.0	5.2
RMnF 700	49.3	3.9	99.2

329

3.4 Batch sorption tests 330

The results of the sorption tests using SCuF on synthetic solutions are shown in Figure 6a. The 331 sorption capacity of SCuF towards manganese from the single metal solution was $16 \pm 1 \text{ mg}_{Mn}/\text{g}_{SCuF}$. 332 Having additional metal ions in solution was associated with a marginal decrease of sorption capacity, 333 though no clear tendency was observed with the competing metal ions. Indeed, the sorption capacity 334

towards manganese was $14\pm 2 \text{ mg}_{Mn}/\text{g}_{SCuF}$ from the Mn+Na solution and 15 ± 1 from the one containing Mn+Li+Na+Co.

The sorption capacity of the same material (SCuF) towards the cobalt contained in different single and multi-metal Co-bearing solutions is shown in Figure 6 b. The sorption capacity from the single metal solution was $4.8\pm0.5 \text{ mg}_{Co}/\text{g}_{SCuF}$. Adding Li or Na produced a slight decrease in the adsorption capacity to 4.4 ± 0.4 and $4.0\pm0.6 \text{ mg}_{Co}/\text{g}_{SCuF}$, respectively. In contrast, a dramatic decrease in sorption capacity down to 0.3 ± 0.1 was observed when the solution contained Co+Li+Na+Mn. These results suggested that Mn and Co most probably compete for the same sites on the surface of SCuF, though the higher selectivity was observed for manganese.

344 The interference of Na and Li ions on Mn adsorption was in general very little, even when these ions 345 were present at high concentration (e.g. Na). A negligible sorption capacity of the Cu-based ferrite towards Li and Na elements was appreciated in these conditions. A previous study highlighted the 346 347 satisfactory chemical stability of CuFe₂O₄ in aqueous media and the formation of a net negative charge on the ferrite surface above pH 6, through point of zero charge (pzc) measurement [24]. 348 349 Similarly, another study associated the adsorption of metal cations onto metal oxides with the generation of negative charges on the ferrite surface (Me-O⁻) in the slightly alkaline environment 350 351 [20].

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Figure 6: Mn sorption on SCuF for Mn (Mn 30 mg/L) and multi-metal solutions: Mn+Li (Mn 30 mg/L; Li 30 mg/L), Mn+Na (Mn 30 mg/L; Na 25 g/L), and Mn+Li+Na+Co (Mn 30 mg/L; Li 30 mg/L; Na 25 g/L; Co 5 mg/L) (a) and Co sorption on SCuF for Co (Co 5 mg/L) and multi-metal solutions: Co+Li (Co 5 mg/L; Li 30 mg/L), Co+Na (Co 5 mg/L; Na 25 g/L), and Co+Li+Na+Mn (Co 5 mg/L; Li 30 mg/L), Xa 25 g/L; Na 25 g/L; Mn 30 mg/L).

The Mn-stripping effluent, after precipitation at pH 8, 9, and 10, was used to test the adsorption capacities of SCuF at the three pHs, while RCuF only at pH 9. The complete removal of Al, Cu and Ni, was observed whereas minor amounts of Co, Li and Mn remained in solution (SI, Table S1).

Figure 7 a and b illustrate the tests performed on pretreated effluents at pH 8, 9, 10, using 2 g/L of suspended SCuF, showing comparable sorption behaviour as in the synthetic solutions, newly indicating the competitions between Mn and Co, with the preferable sorption of Mn. The higher relative amount in solution of Mn with respect to Co might be responsible for the preferential Mn uptake in these experiments and on synthetic solution.

A gradual decrease for the capacities as the relative concentrations of solubilized metals (Mn; Co) in 368 369 solution diminished and pH increased, was observed, also appreciable from the removal efficiencies. Using RCuF on Mn-stripping effluent, after precipitation at pH 9 produced a slight increase in metals 370 371 sorption, resulting in a sorption capacity of 13±1 and 0.25±0.05 mg/g_{ferrite} towards Mn and Co (vs 372 12±1 and 0.21±0.01 by SCuF), respectively. In terms of metal removal, the RCuF at pH 9 373 immobilized all Mn and about 70% of Co, whereas the SCuF removed 91% of Mn and 59% of Co 374 Figure 7 a and b depict the sorption on pretreated effluent for Mn and Co, respectively. This might be correlated to a dual factor: the different chemical composition (although the two samples behave 375 similarly) or, most likely, to the larger specific surface area of RCuF. The measured concentrations 376 377 of metals in solutions before and after ferrite sorption tests are resumed in supplementary information,

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Figure 7: Mn (a) and Co (b) sorption capacities ($mg/g_{ferrite}$) and removal efficiency (%) on real LIB effluent after pre-treatment at pH 8, 9, and 10 with SCuF and RCuF only at pH 9).

382 **4. Conclusions**

In this study different advanced hydrothermal syntheses have been employed to prepare nanosized magnetic sorbents from Fe-sludge and the Mn-stripping effluent. The first meaningful outcome is that these secondary streams can be profitably reused as metal source for such purpose.

The physical- and chemical properties of the final ferrite products depended on the selected combination (dissolution, ultrasound dissolution, coprecipitation conditions, mixing time, capping agent, microwave/autoclave hydrothermal, post-precipitation ultrasound, sintering) and conditions (time, temperature, etc.) of treatments and on starting materials.

The autoclave synthesized Cu-based ferrites showed comparable nanosized morphology and sorption properties, though the chemical composition of recycled Cu-based ferrite was significantly different from reference CuFe₂O₄. Both Cu-based ferrites showed small crystallite size (<20 nm) with a narrow particle size distribution, specific surface >160 m²g⁻¹ and similar magnetic behavior. Furthermore, Cu-based ferrites used as sorbent media on synthetic and real effluent solutions evidenced a pronounced affinity for Mn in presence of Co, Li and Na as interfering ions. Likely, Co and Mn interact with the same superficial sites onto ferrite, generated in alkaline conditions.

For simultaneous reuse of Fe-sludge and Mn-stripping effluent, the synthetic route with autoclave was inefficient to obtain nanosized powders, while adopting ultrasounds to promote the direct dissolution of Fe-sludge through Mn-stripping solution and a MW hydrothermal treatment, highly crystalline ferrite compounds were achieved.

The obtained Mn-Co-Ni ferrites revealed considerable crystallite size distribution although larger crystallites were below 100 nm. The sintering temperature (100 vs 700 °C) strongly influenced the magnetic properties and the morphology of nanograins (*e.g.* crystal size: 57 nm at 100 °C to 98 nm to 700° C; morphology: partial rearrangement from cubic-like to rhombohedral; magnetic saturation: 27.1 emu g⁻¹ at 100 °C to 49.7 emu g⁻¹ at 700 °C).

- 406 Unfortunately, these latter compounds haven't been tested as sorbent materials yet. On the other hand,
- 407 the recycled $Mn_{(0.63)}Co_{(0.35)}Ni_{(0.02)}Fe_2O_4$, quaternary transition metal mixed ferrite, may offer
- promising application as new electrode material [4,12].

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517 Supplementary material



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Figure S1: SEM image of RMnF HT

520 Table S1: metal content after precipitation pre-treatment and after sorption tests with SCuF and RCuF

Post precipitation						
(mg/L)	Со	Li	Mn			
pH 8	5.4	27.3	81.3			
рН 9	0.7	26.3	25.6			
рН 10	0.5	23.6	3.5			
Post sorption						
(mg/L)	Со	Li	Mn			
pH 8 - SCuF	4.0±0.2	27.3±0.3	49±1			
pH 9 - SCuF	0.3±0.1	25.7±0.9	2.3±0.5			
pH 9 - RCuF	0.2	25±1	<lod< th=""></lod<>			
pH 10 - ScuF	0.1 ± 0.1	22.9±0.6	<lod< th=""></lod<>			

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