



Statistical analysis of the effect of the electrochemical treatment and the acid concentration on the leaching of NMC cathodes from spent Li-ion batteries

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ABSTRACT

Electric mobility has sharply increased the demand for batteries, making a European priority their sustainability throughout their entire lifecycle. However, battery recycling still needs to be improved, since it relies on industrial processes that require high amounts of energy, are not selective and require chemical reagents such as concentrated acids and reducing agents. In this work, the effect of acid concentration and electrochemical treatment on the leaching of Li, Ni, Mn, Co from electric vehicle $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) batteries was studied at room temperature. A factorial 3^2 experimental design was considered to deconvolve the effect of the chemical leaching from the electrochemical treatment in NMC batteries. An analysis of the variance was performed to determine which factors have a statistically significant effect on the initial leaching rate and the final leaching yield of each one of the metals. The main advantage and novelty of this work is that the combination of the electrochemical treatment and the acid concentration is proved to be significant for the extraction yield of the metals contained in Li-ion batteries of NMC cathode. All the experiments have been done in galvanostatic mode, with no pre-treatments and at room temperature with no addition of reducing agents. Based on the results obtained from the statistical analysis, a novel environmentally friendly process for recycling the cathodes of spent batteries was proposed. This 3-sequential-step process would allow to recover separately the Al foil, the Li fraction, the Mn fraction, and the Ni-Co fractions.

1. Introduction

Electric vehicles (EVs) are expected to play an essential role in the reduction of greenhouse gas (GHG) emissions from the transport sector and as an opportunity to replace fossil fuels to limit global warming [1]. Global annual sales of EVs are expected to grow to nearly 26 million units by 2030 and take over internal combustion engine cars before 2040 [2,3]. By 2030, Lithium-Ion Batteries (LIBs) will likely make up 80% of the 160,000 metric tons of the annual global lithium demand [4]. In addition, by that year, roughly 3 million metric tons of LIBs will be reaching their End Of Life (EOL). Improper management of these LIBs, which are considered a hazardous waste, would cause a serious

environmental problem due to the accumulation of toxic materials such as metals, organic electrolytes, binders, and plastics contaminating soil, air and groundwater [5]. In this context, ensuring a sustainable EOL batteries management should be a priority to reduce GH emissions [6].

Battery recycling also addresses geopolitical supply risks, especially for countries with no raw material reserves. Lithium has been included in the 2020 EU list of Critical Raw Materials (CRM) [7] and given the exponential demand of EV LIBs, there will be challenges to meet the demand for raw materials. This demand could be alleviated by the recovery of these materials from spent LIBs [8]. Besides, recycling EOL batteries has a considerable business potential [9] and would contribute to meet the global demand by exploiting both, primary and secondary,

Abbreviations: ANOVA, Analysis Of Variance; CRM, Critical Raw Materials; DF, Degrees of Freedom; DI, Deionized; EOL, End Of Life; EVs, Electric Vehicles; GHG, Greenhouse gas; LIBs, Li-Ion Batteries; MMO, Mixed Metal Oxides; NMC, $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$.

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material sources [10]. The main routes for LIBs recycling are pyrometallurgy, hydrometallurgy, bio-hydrometallurgy, and direct recycling. All these processes require several unit operations and pre-treatments for the full recovery of the different materials. Direct recycling, also known as mechanical recycling, has a low environmental impact but requires a complete and flawless separation of cathode materials and is limited to one chemistry, hindering its industrial scalability [11]. Pyrometallurgy consists in smelting the whole battery at high temperatures (~1500 °C) to recover a low-purity alloy of valuable metals (Ni, Co, Cu) which have to be further refined via hydrometallurgy. Li cannot be recovered by the pyrometallurgical route unless the slag undergoes further refining processes [12]. Lombardo's group demonstrated that incineration could be used as a pre-treatment for hydrometallurgical recycling [13]. According to the authors, the advantage of this strategy is that it eliminates the organic components that can be a problem in subsequent leaching steps.

Hydrometallurgy involves leaching metals by using chemical reagents such as strong acids [14] and/or solvents and it is usually preferred because of its lower energy costs, lower GHG emissions and higher purities of the recycled metals [15]. Among the inorganic acids conventionally used in hydrometallurgy, hydrochloric acid shows excellent efficiency, however, Cl_2 is produced leading to potential environmental and health and safety problems [16]. Other inorganic acids such as nitric [17], phosphoric [18], sulphuric [19,20] and hydrofluoric [21] acids have been used in numerous works with good recovery yields [22]. Lithium recovery from spent LIBs has also been reported in literature by using a mixture of solvents [23]. The common practice to recycle LIBs via hydrometallurgy consists in leaching the metals contained in the battery using concentrated sulphuric acid with a reducing agent, generally hydrogen peroxide [14,24]. The strength of the Co(III)-O and Mn(IV)-O chemical bonds [25] hinders the solubilization process. The addition of a reducing agent enhances the leaching efficiency of spent LIBs as the solubilities of Co^{2+} and Mn^{2+} are higher than Co^{3+} and Mn^{4+} solubilities, respectively [26]. Reducing agents such as hydrogen peroxide and ascorbic acid [27], glucose [28], cellulose and sucrose [29] have been reported in the literature. Hydrogen peroxide is the main reducing agent used in the literature, although its instability in acidic solution and the complexity of the subsequent metal purification process, have led to a search for alternative leaching reducing agents and methods. For example, a novel method for Li leaching has been explored by Makuza et al. [30]. The method consists in a carbothermal reduction roasting at 600 °C followed by a carbonated ultrasound-assisted water leaching and further recovery of transition metals with 4 M sulphuric acid without a reducing agent.

Two recent, and deemed greener, options are bio-hydrometallurgy and organo-leaching. On the one side, bio-hydrometallurgy consists in a leaching process assisted direct or indirectly by bacteria [31]. On the other side, organo-leaching consists in leaching using organic acids such as citric [32], oxalic [33], malic [34], tartaric acid [35] or biomass assisted leaching [36]. Recoveries with these methods are comprised between 80% and 90%, working at 80–90 °C for 1–5 h. However, these technologies are still far from being industrially ready [37].

Other environmentally friendly alternatives have been sought through electrochemical treatments, which involve the use of electricity to cause specific reactions [38–40]. One example of electrochemical recycling of LiCoO_2 batteries has been reported in the literature [41] using the following conditions: 70 °C, 2.5 M malic acid and an applied voltage of 8 V. Co and Li were recovered with leaching efficiencies after 2 h of 96% and 97%, respectively. Another example was reported by Meng et al. for a LiCoO_2 battery using 1.5 M malic acid and 70 °C with a recovery of 94% and 90% for Li and Co, respectively [42]. An example of indirect electrochemical treatment was presented by Fang et al. [43]. The reported procedure consists in two steps. In the first one, the Al foil is leached using the sodium hydroxide generated by the electrolysis of sodium sulphate. Subsequently, the remaining powder is leached with sulphuric acid also obtained from sodium sulphate electrolysis and 2% hydrogen peroxide at 60 °C.

X. Chen et al. [44] reported the detachment of the aluminium foil using an ultrasonic acid scrubbing with 0.1 M sulphuric and oxalic acids. An additional study of electrochemical recycling for LIBs has been reported by Q. Meng's group for the recovery of Li, Ni, Mn and Co. In Q. Meng's work [45] an electrochemical treatment using 1.25 M malic acid, 8 V, and 60 °C was applied after dissolving the Al foil with sodium hydroxide and calcining the cathode material at 650 °C to burn the binder. Finally, the cathodic material was ground and extruded in an epoxy mould for its use as a working electrode with an overall leaching efficiency of > 99% for all metals. K. Liu group [46] used a 2.5 g/L ammonium sulfate solution and anodic electrochemical treatment to recover Li from a $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) battery. To prepare the battery, the material was immersed in dimethyl carbonate and dried at 80 °C for 12 h. After that, electrolysis was carried out at 25 V and 80 °C recovering 98% of the Li and the Al foil in less than 10 min.

The goal of this work is to study the effect of the acid concentration and the electrochemical treatment on the leaching rate and the leaching yield of NMC EV commercial battery cathodes. There are studies in the literature that evaluate the chemical leaching and the electrochemical leaching of Li-ion cathodes but using organic acids, dissolving Al foil and calcining the cathodic material prior to the tests. Besides, the authors are not aware of studies in which the effect of the chemical leaching is deconvolved from the effect of the electrochemical leaching. The novelty of this work lies in discerning the effect of the electrochemical process from the chemical leaching at room temperature for NMC cathodes through the Analysis Of Variance (ANOVA) with no pre-treatments on the cathodic foil and at room temperature. A fully randomized factorial experimental design was considered, and an ANOVA was used to assess if the considered factors and their interactions had a statistically significant effect on the leaching process of the different elements of the cathode of the EV battery. Based on the results, a novel and environmentally friendly strategy was proposed for extracting selectively different valuable elements contained in the NMC cathodes. The process is done at room temperature, at low voltages (2–15 V), with neutral and mildly acid media and no pre-treatments. These findings open the door for practical scaling-up solutions.

2. Materials and methods

2.1. Materials

Sodium sulfate anhydrous for analysis, (Na_2SO_4 , PanReac, ACS reagent >99,0%) and Sulfuric Acid (H_2SO_4 96%, PanReac, ACS reagent) for analysis were used as received. All the reagents were stored at room temperature. Electrolytes were prepared with Deionized (DI) Type 2 water that was obtained from an ELGA-VEOLIA purification system (Resistivity: 1 $\text{M}\Omega\cdot\text{cm}$ at 25 °C; TOC: <50 ppb) and was always freshly prepared just before its use. Samples for ICP analysis were prepared using Type 1 ultrapure water obtained from a Milli-Q purification system (Resistivity: 18.2 $\text{M}\Omega\cdot\text{cm}$ at 25 °C; TOC: <5 ppb) and were stored at 5 °C prior to their analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) using the PerkinElmer OPTIMA 2000™ spectrometer with dual-view optics and a 160–900 nm spectral range.

2.2. Battery disassembly

The NMC Li-ion battery used in this work was a 40-kWh battery pack extracted from an EV at its end of use. The spent battery was discharged by submerging it in a saline solution at room temperature for 24 h. The battery's hard case was disassembled, and the Aluminium soft casing was removed (Fig. S1). Inside each module, there are 4 cells and their polymeric unions which were separated to access the different electrodes. Connections were manually cut and the cells from the module were isolated and opened to recover the anodes (with a Cu current collector) and the cathodes (with an Al current collector). Each cell is

composed of 18 anodes and 17 cathodes. Cathodic and anodic sheets were separated and dried in a fume hood at ambient temperature for 24 h. The smooth surface of the cathode can be seen in (Fig. S2). These cathodic foils were cut and directly used with no further chemical or thermal pre-treatments in the leaching experiments.

2.3. Elemental analysis of the cathodic foils

Elemental analysis of the cathodic foils was done by duplicate. The analysis was done by aqua regia digestion followed by an analysis by ICP-OES using a PerkinElmer OPTIMA 2000™ spectrometer with dual-view optics and a 160–900 nm spectral range. The elemental composition of the cathodes used as a reference to calculate leaching rates and yields is shown in Table S1 of SI.

2.4. Leaching experiments

A series of leaching experiments were conducted in different conditions: with different electrochemical treatments and acid concentrations (Table 1).

The cathodic foils obtained from the battery disassembly were cut into small and uniform square pieces of 1×1 (cm x cm). In each leaching experiment, one of these pieces was placed between two 0.9×6 (cm x cm) MMO (Mixed Metal Oxides) mesh electrodes. The piece was fixed to the MMO mesh using a conductive adhesive (carbon double-sided tape, Nisshin-em NEM tape) at the side which does not face the counter electrode while the rest of the MMO surface was covered with Teflon (Fig. S3.b).

A 2.5×5 (cm x cm) Ti-Pt mesh was used as counter electrode and set in front of the working electrode with an inter-electrode distance of 1 cm. In the experiments that required a power source, a Velleman LABPS3030SM 0–20 and 0–30 V DC power source was used. The working electrode was connected either as anode or cathode according to the experiment (Table 1). All the experiments were done in galvanostatic mode at 0.5 A.

The leaching was carried out in a 100 mL beaker, 0.05 g of cathodic foil in 80 mL solution and homogenized by a Teflon-coated magnetic stirrer at 450 rpm. All tests were performed and maintained at 25 °C using a jacketed vessel connected to a DYNEO DD-600 F thermostatic bath.

In all the experiments, the leaching was monitored for 4 h. Solution pH, temperature and redox potential were monitored with a Thermo Scientific Eutech meter using a pH probe and TPS SmartCHEM Lab redox probe with an Ag/AgCl reference electrode. Samples were taken at different times: 0 (initial solution) and at 1, 5, 10, 15, 30, 60, 120, 180 and 240 min. For each sample, 0.5 mL were taken from the leaching reactor and diluted up to 10 mL with Milli-Q ultrapure water. Samples were stored up to 3 days in a refrigerator (5 °C) before analyzing them. The concentration obtained at each time was used to calculate the leaching yield of each metal as described in Section 2 of SI. The concentration of different metals (Li, Ni, Mn, Co) in the samples was determined by ICP-OES.

Table 1

Experimental design considered in this work. A 3^2 factorial design with one replicate. The experimental design leads to a total number of experiments of 18.

Experiment	Acid concentration	Electrochemical treatment
1	0.0 M	None (Chemical leaching)
2	0.0 M	Anodic
3	0.0 M	Cathodic
4	0.5 M	None (Chemical leaching)
5	0.5 M	Anodic
6	0.5 M	Cathodic
7	2.0 M	None (Chemical leaching)
8	2.0 M	Anodic
9	2.0 M	Cathodic

2.5. Statistical analysis

A full 3^2 factorial design with 1 replication was used in this work. In such study, 2 factors (electrochemical treatment and acid concentration) were considered at 3 different levels. This experimental design leads to 18 experiments.

On the one side, the acid concentration factor is a continuous numerical factor which was considered in this work at 3 different levels: 2 M, 0.5 M and 0 M (i.e. using Na_2SO_4 to achieve similar ionic strengths in all the experiments). On the other hand, the electrochemical treatment factor is a categorical factor. The 3 levels of this factor that were considered in this work were: no electrochemical treatment (i.e. just chemical leaching), anodic treatment and cathodic treatment. The order of the experiments was completely randomized in order to orthogonalize the considered factors with the order factor (in order to avoid confusing time-drift effects with factor effects) and all experiments were performed under the same conditions with controlled temperature.

Table 1 sums up all the experiments defined by the experimental design considered in this work. The three different response variables considered for each one of the metals (Li, Ni, Mn, and Co) are: the initial extraction yield, the initial leaching rate, and the final extraction yield. First, the initial extraction yield of a given metal was defined as the fraction of the metal that has leached after 1 min. This parameter quantifies the metal that is loosely linked to the solid, and therefore that dissolves nearly immediately after introducing it in the solution. Second, the initial leaching rate was defined as the initial slope of the time-evolution curve of the extraction during the first 5 min of reaction. Finally, the final extraction yield of a given metal was defined as the fraction of that metal that has leached by the end of the experiment (i.e. after 4 h). An example of the considered response variables on the Lithium plot can be found in SI (Fig. S4), as well as the equations that define the response variables (Eq. S1 – S6).

ANOVA was performed in order to determine which factors have a statistically significant effect on each of the 12 considered response variables. Each one of the performed ANOVA analyses was validated before accepting the obtained results. The validation consisted in assessing if four main hypotheses were met: independence, statistical significance, residue normality and homoscedasticity. First, independence is ensured by the selected experimental design (i.e., a balanced orthogonal and randomized design). Secondly, statistical significance is fulfilled when the residual number of degrees of freedom (DF) is higher than 4. Since in this study DF range from 14 to 17 (Tables 2 to 10), the statistical significance hypothesis can be considered to be met in all the ANOVA studies presented here. Thirdly, residue normality was assessed using normal probability plots and normality tests (Kolmogorov–Smirnov test and Shapiro–Wilk test). Finally, homoscedasticity was checked using residue versus predicted plots. All the statistical analyses were performed with Statgraphics Centurion 18, with a 95% confidence level.

Table 2

ANOVA table for the effect of the acid concentration (factor A) and the electrochemical treatment (factor B) on the Li initial leaching rate.

Source	Sum of Squares	DF	Mean Square	F-Ratio	P-Value
Main effects:					
A	27.7592	1	27.76	10.9067	0.0080
B	58.109	2	29.05	11.4156	0.0026
Interactions:					
AB	25.771	2	12.89	5.06276	0.0303
Residual	25.4515	10	39.35		
Total	146.558	16			

Table 3

ANOVA table for the effect of the acid concentration (factor A) and the electrochemical treatment (factor B) on the Li final extraction yield.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Main effects:					
A	1315.32	1	1315.32	8.31722	0.0163
B	4304.99	2	2152.49	13.611	0.0014
Interactions:					
AB	4801.25	2	2400.62	15.18	0.0009
Residual	1581.44	10	158.14		
Total	13867.1	16			

Table 4

ANOVA table for the effect of the acid concentration (factor A) and the electrochemical treatment (factor B) on the Co initial leaching rate.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Main effects:					
A	1.88328	1	1.88328	21.3447	0.0007
B	0.639276	2	0.31968	3.6227	0.0618
Interactions:					
AB	0.882374	2	0.44118	5.00031	0.0285
Residual	0.970551	11	0.08821		
Total	4.22099	17			

Table 5

ANOVA table for the effect of the acid concentration (factor A) and the electrochemical treatment (factor B) on the Co final extraction yield.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Main effects:					
A	1812.4	1	1812.4	100.4	0.0010
B	151.376	2	75.6	4.19284	0.0443
Interactions:					
AB	384.34	2	192.1	10.6455	0.0027
Residual	198.569	11	18.1		
Total	2499.09	17			

Table 6

ANOVA table for the effect of the acid concentration (factor A) and the electrochemical treatment (factor B) on the Ni initial leaching rate.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Main effects:					
A	0.51892	1	0.51892	86.7741	0.0010
B	0.150718	2	0.07536	12.6016	0.0034
Interactions:					
AB	0.0850018	2	0.04250	7.10703	0.0168
Residual	0.0478409	8	0.00598		
Total	0.925773	14			

Table 7

ANOVA table for the effect of the acid concentration (factor A) and the electrochemical treatment (factor B) on the Ni final extraction yield.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Main effects:					
A	2054.27	1	2054.27	69.3895	0.0010
B	76.2546	2	38.13	1.28787	0.3144
Interactions:					
AB	477.586	2	238.79	8.06598	0.0070
Residual	325.655	11	29.61		
Total	2886.86	17			

Table 8

ANOVA table for the effect of the acid concentration (factor A) and the electrochemical treatment (factor B) on the Mn initial leaching rate.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Main effects:					
A	3.94964	1	3.94964	107.25	0.0010
B	1.10173	2	0.55086	14.9584	0.0010
Interactions:					
AB	0.181163	2	0.09058	2.4597	0.1353
Residual	0.368263	10	0.03682		
Total	5.17509	16			

Table 9

ANOVA table for the effect of the acid concentration (factor A) and the electrochemical treatment (factor B) on the Mn final extraction yield.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Main effects:					
A	1025.92	1	1025.92	119.325	0.0010
B	76.3415	2	38.17	4.43964	0.0417
Interactions:					
AB	197.126	2	98.56	11.4638	0.0026
Residual	85.9772	10	8.60		
Total	1395.29	16			

Table 10

Optimum configurations to maximize the initial leaching rate and the final extraction yield, for each element.

	Initial leaching rate		Final extraction yield	
	Acid concentration	Electrochemical treatment	Acid concentration	Electrochemical treatment
Li	High	None	Low	Anodic
Co	High	Cathodic	High	Cathodic
Ni	High	Anodic	High	Cathodic
Mn	High	Anodic	High	Cathodic

3. Results and discussion

3.1. Lithium

3.1.1. Li Initial extraction yield

Neither of the factors (nor the electrochemical treatment, nor the acid concentration) has a statistically significant effect (with a 95% significance level) on the initial extraction yield of Li (Fig. S5). This suggests that the Li that is initially leached to the solution might be the remaining of the battery electrolyte, still present on the surface of the foil since no pre-treatments were done to clean the battery cathode's surface.

3.1.2. Li Initial leaching rate

Both, the electrochemical treatment and the acid concentration have a statistically significant (at a 95% confidence level) effect on the Li initial leaching rate (Fig. 1.a., Table 2). On the one side, the Li initial leaching rate increases when the acid concentration is increased (Fig. 1. c.). On the other side, the anodic electrochemical treatment leads to the highest Li initial leaching rate; followed by the chemical leaching (i.e., no electrochemical treatment); to finish with the cathodic treatment which presents the slowest Li initial rate both at acid and neutral conditions (Fig. 1.d.).

In addition, the interaction between both factors is also significant (at a 95% confidence level) (Fig. 1.a., Table 2). Therefore, the effect of one of the factors depends on the level of the other factor. The combination of factors that leads to the quickest initial leaching of Li is chemical leaching (i.e., no electrochemical treatment) with the most

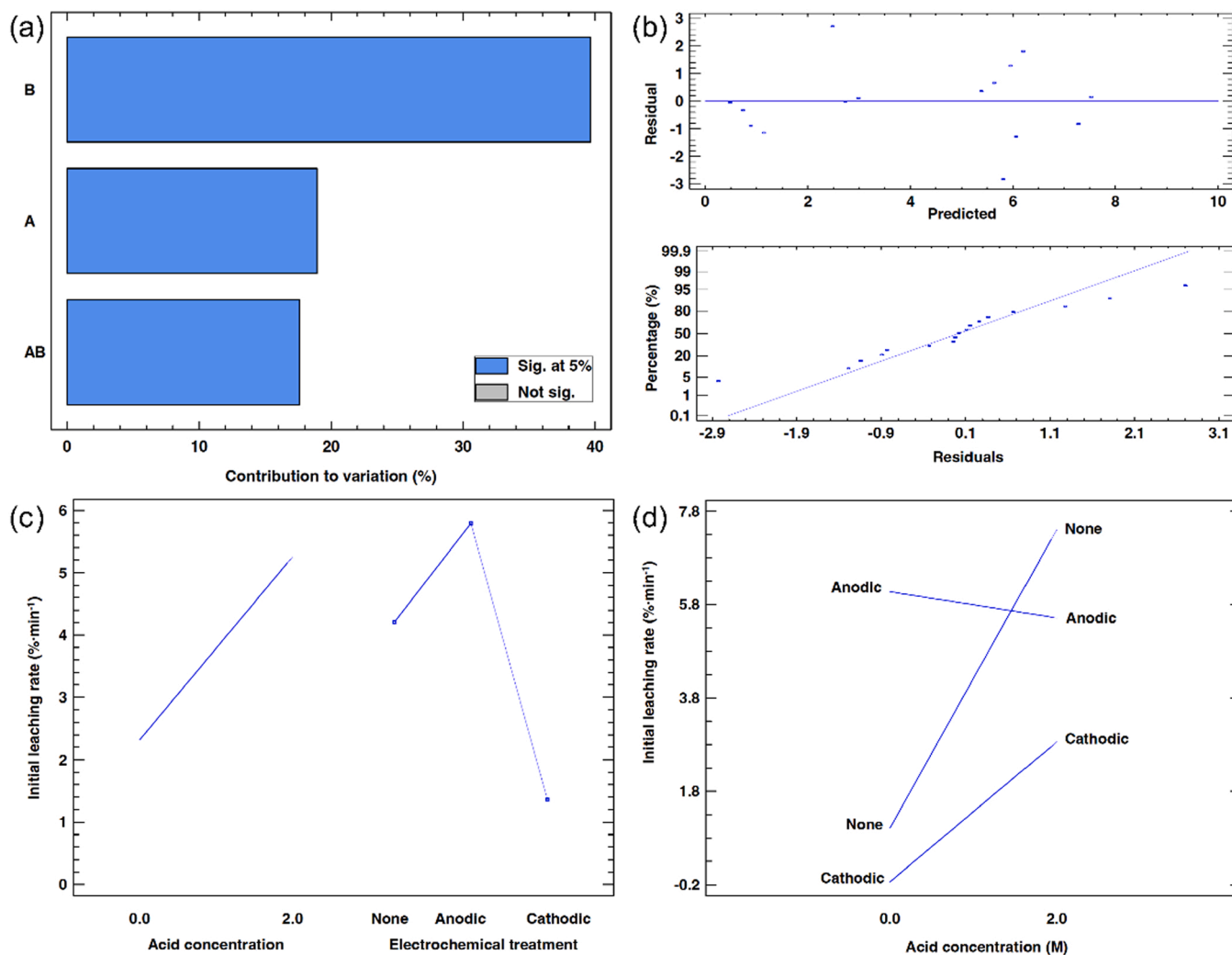


Fig. 1. Statistical analysis of the effect of the acid concentration (Factor A) and the electrochemical treatment (Factor B) on the Li initial leaching rate. (a) Pareto chart, (b) validation plots (residual versus predicted plot, and normal probability plot of the residuals), (c) main effects plot, and (d) interaction plot. Study validated by (b) as the residuals are distributed without defined structure and with a linear pattern at the normal probability plot.

concentrated acid (2 M H₂SO₄). At high acid concentrations, the application of an electric current hinders the leaching process, possibly due to the onset of parasitic reactions (such as the oxygen evolution reaction in the anode, and the hydrogen evolution reaction in the cathode). On the contrary, in Na₂SO₄, the application of an anodic current improves the Li initial leaching rate in comparison to chemical leaching (i.e., no current applied). This fact may be due to the electrostatic attraction of Li ions by the negatively charged cathode that causes a Li migration from the anode to the cathode [47]. This Li migration generates a Li concentration gradient, that increases the leaching rate of Li. Finally, the cathodic treatment slows the Li initial leaching regardless of the acid concentration, possibly due to the negative charge of the cathode that therefore attracts Li ions, hindering in this way the leaching process.

3.1.3. Li final extraction yield

Both, the electrochemical treatment and the acid concentration, have a significant effect (at a 95% confidence level) on the Li final extraction yield with a very strong interaction (Fig. 2.a., Table 3). The combination of factors that achieves the highest Li final extraction yield is the anodic electrochemical treatment without acid (Na₂SO₄). On the one hand, during the anodic treatment, the negative charge of the cathode and the positive charge of the anode cause the migration of Li ions from the anode to the cathode, similarly to what happens during the discharge process of a battery. The Li migration favours the leaching process,

improving the final Li extraction yield. On the other hand, the neutral electrolyte (Na₂SO₄) promotes the selective leaching of Li, improving the Li final extraction yield. The strong interaction between both factors is due to the hindrance of Li leaching by the onset of gas evolution reactions when the electrochemical treatment is carried out with an acidic electrolyte. After the anodic treatment in Na₂SO₄ electrolyte, the following highest Li final extraction yield is obtained for the chemical leaching with the most concentrated acid (i.e. 2.0 M H₂SO₄). This can be due to the destabilizing effect of the acid on the layered structure of the cathodic foil that destroys the molecular structure of the NMC battery, releasing Li [42]. The anodic treatment in Na₂SO₄ leads to substantially larger (nearly 20% greater) Li final extraction yields than the chemical leaching in concentrated acid (Fig. 2.d.).

3.2. Cobalt

3.2.1. Co initial extraction yield

Neither the acid concentration nor the electrochemical treatment have a statistically significant effect (with a 95% significance level) on the initial extraction yield of Co (Fig. S6). In none of the performed experiments, a significant amount of Co was detected initially in the electrolyte. This suggests that there is no loose Co in the battery cathodic foil. Therefore, all the Co extracted during the experiments is due to the performed treatment.

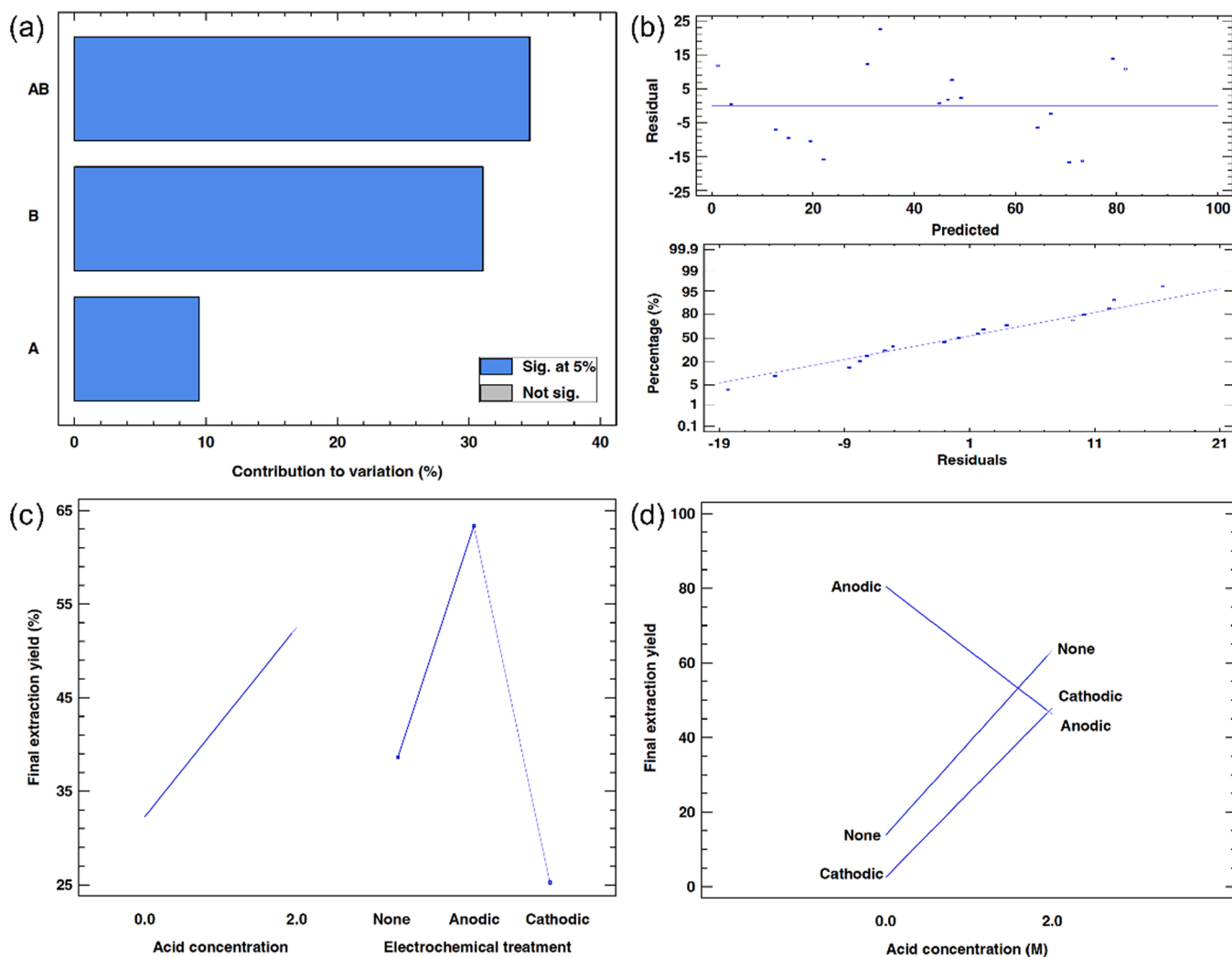


Fig. 2. Statistical analysis of the effect of the acid concentration (Factor A) and the electrochemical treatment (Factor B) on the Li final extraction yield. (a) Pareto chart, (b) validation plots (residual versus predicted plot, and normal probability plot of the residuals), (c) main effects plot, and (d) interaction plot. Study validated by (b) as the residuals are distributed without defined structure and with a linear pattern at the normal probability plot.

3.2.2. Co initial leaching rate

Both, the acid concentration and the interaction of the acid concentration and the electrochemical treatment have a statistically significant effect (at 95% confidence level) on the Co initial leaching rate (Fig. 3.a., Table 4). An increase in acid concentration leads to an increase of the Co initial leaching rate (Fig. 3.c.), especially if combined with an electrochemical treatment: the cathodic treatment displays slightly faster Co initial leaching rates than the anodic one (Fig. 3.d.). The higher Co leaching rates obtained when an electrochemical treatment is applied, in comparison to chemical leaching, suggests that the charge compensation by cationic and anionic redox reactions boosts the Co chemical leaching triggered by concentrated acid [25,26].

3.2.3. Co final extraction yield

Both factors, acid concentration and electrochemical treatment, have a statistically significant (at a 95% confidence level) effect on the Co final extraction yield (Fig. 4.a., Table 5). On the one hand, the final extraction yield increases when the acid concentration is increased (Fig. 4.c.). On the other hand, the cathodic electrochemical treatment leads to the highest Co extraction yield (Fig. 4.c.). The interaction between both factors is also significant (at a 95% confidence level, Fig. 4. a., Table 5), showing that there is a synergistic effect between the acid concentration and the electrochemical treatment. The highest Co final

extraction yield is obtained with a cathodic electrochemical treatment with the most concentrated acid (2 M H_2SO_4 , Fig. 4.d.). On the one hand, the concentrated acid is necessary in order to destroy the molecular structure of the NMC battery cathode, releasing the transition metals. On the other hand, the cathodic electrochemical treatment reduces the insoluble Co(III) present in the battery cathode structure, into soluble Co(II) [25,26]. The combination of the structure destruction by the concentrated acid, and the reduction of Co(III) to Co(II) by the cathodic electrochemical treatment, maximizes the Co final extraction yield.

3.3. Nickel

3.3.1. Ni Initial extraction yield

Neither of the factors (nor the electrochemical treatment, nor the acid concentration) has a statistically significant effect (with a 95% significance level) on the initial extraction yield of Ni (Fig. S7). Furthermore, no significant presence of Ni (<5%) was found in the initial sample of any of the experiments. This suggests that there is no loose Ni in the battery cathodic foil. Therefore, all the Ni extracted during the experiments is due to the performed treatment.

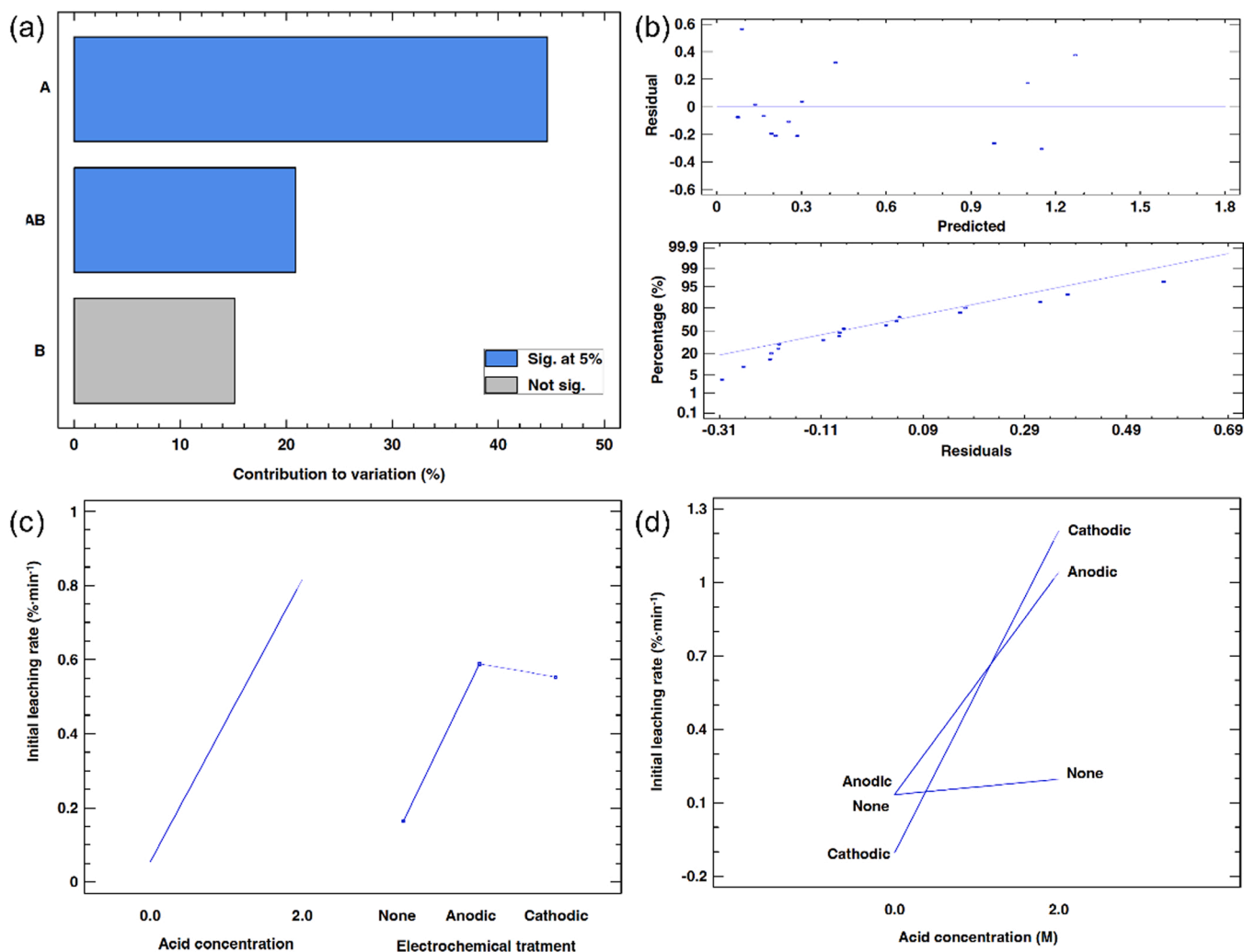


Fig. 3. Statistical analysis of the effect of the acid concentration (Factor A) and the electrochemical treatment (Factor B) on the Co initial leaching rate. (a) Pareto chart, (b) validation plots (residual versus predicted plot, and normal probability plot of the residuals), (c) main effects plot, and (d) interaction plot. Study validated by (b) as the residuals are distributed without defined structure and with a linear pattern at the normal probability plot.

3.3.2. Ni Initial leaching rate

Both factors and their interaction have a significant (with a 95% significance level) effect on the Ni initial leaching rate (Fig. 5.a., Table 6). The most significant effect on the initial Ni leaching rate (Table 6), is due to acid concentration. The anodic electrochemical treatment improves the Ni initial leaching rate, for all the acid concentrations, whereas the cathodic treatment only improves slightly the Ni initial leaching rate with respect to the chemical leaching (Fig. 5.c.). This behavior suggests that Ni initial leaching is promoted on the one side by concentrated acidic media and on the other side, with a weaker effect, by the redox anodic oxidation reactions. Both, the acidic media and the gas evolution reactions, have the same effect: they destroy the foil's structure, facilitating the Ni leaching process [45,48]. In contrast with Co, in the Ni case, the cathodic treatment does not improve the initial leaching rate, since the Ni's valence remains the same during the leaching process [49].

3.3.3. Ni final extraction yield

Ni final extraction yield is significantly affected (with a 95% significance level, Table 8) by the acid concentration and by the electrochemical treatment since the interaction term is significant (Fig. 6.a.). Higher acid concentrations lead to higher Ni final extraction yields, for all the electrochemical treatments. At high acid concentrations, the cathodic treatment yields to highest Ni final extraction (Fig. 6.d.). The

electrochemical treatment as an individual factor does not have a significant effect on Ni extraction yield, which may be due to the fact that the Ni's valence remains constant (i.e. Ni(II)) during the leaching process. However, the cathodic electrochemical treatment at high acid concentration results in the highest final extraction yield for Ni, suggesting that the reduction process that promotes Co and Mn leaching (see Sections 3.2.3 and 3.4.3), causes a restructuring of the layered battery cathodic foil which makes easier the release of Ni into the electrolyte [45,48]. This restructuring is not immediate and takes time to happen, which explains why the cathodic treatment improves the Ni final extraction yield but does not improve the Ni initial leaching rate.

3.4. Manganese

3.4.1. Mn initial extraction yield

Neither of the factors (nor the electrochemical treatment, nor the acid concentration) has a statistically significant effect (with a 95% significance level) on the initial extraction yield of Mn (Fig. S8). Furthermore, no significant Mn presence was detected in the initial samples (i.e. first minute) in any of the experiments. This suggests that there is no loose Mn in the battery cathodic foil. Therefore, all the Mn extracted during the experiments is due to the performed treatment.

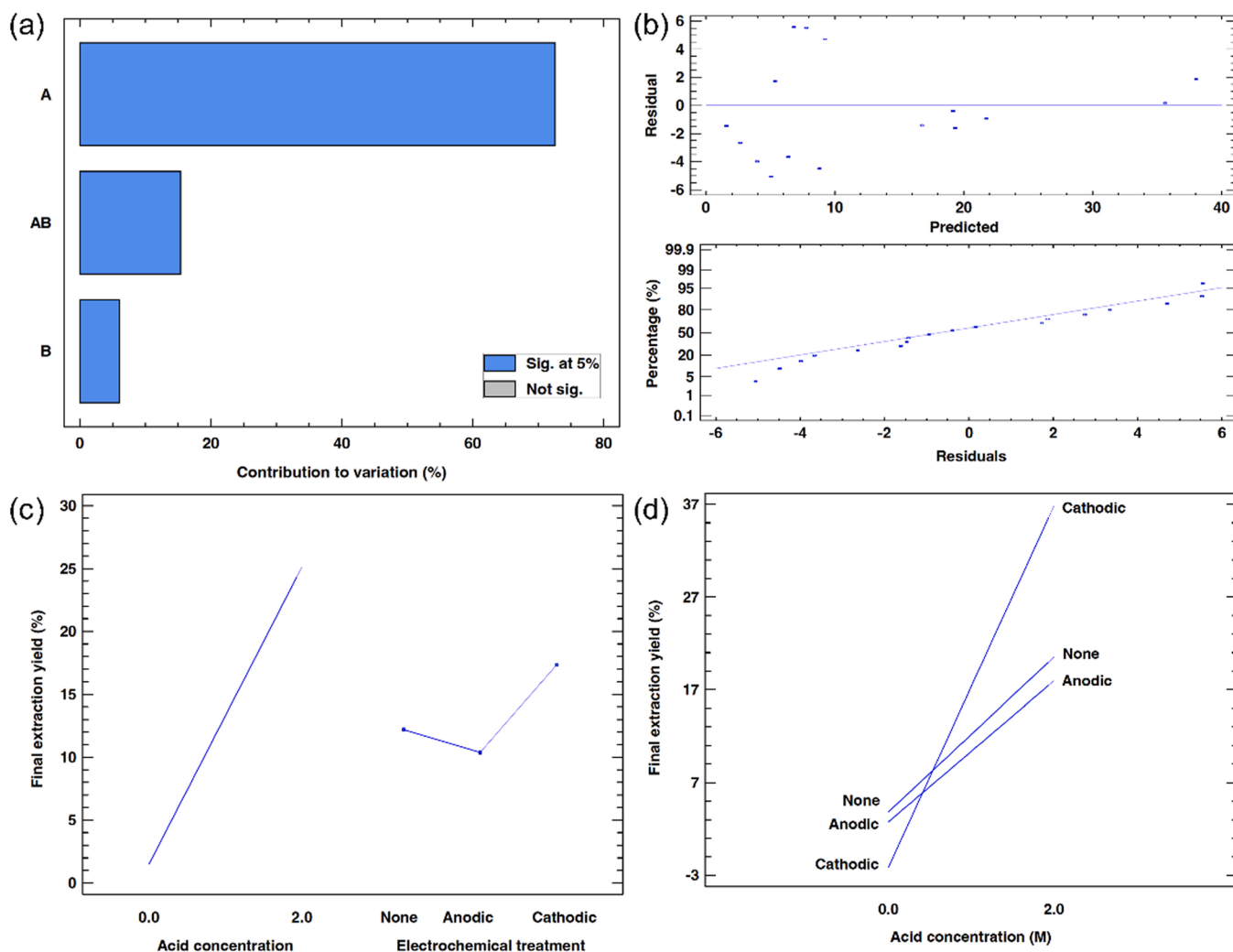


Fig. 4. Statistical analysis of the effect of the acid concentration (Factor A) and the electrochemical treatment (Factor B) on the Co final extraction yield. (a) Pareto chart, (b) validation plots (residual versus predicted plot, and normal probability plot of the residuals), (c) main effects plot, and (d) interaction plot. Study validated by (b) as the residuals are distributed without defined structure and with a linear pattern at the normal probability plot.

3.4.2. Mn initial leaching rate

Both, the electrochemical treatment and the acid concentration, have a statistically significant (at a 95% confidence level) effect on the Mn initial leaching rate (Fig. 7.a., Table 8). On the one hand, an increase in acid concentration leads to a greater Mn initial leaching rate (Fig. 7.c.). On the other hand, for the 2 M H₂SO₄, the anodic electrochemical treatment results in the highest Mn initial leaching rate, followed by the chemical leaching with no electrochemical treatment, ending with the cathodic treatment which presents the lowest Mn initial leaching rate (Fig. 7.d). The interaction between both factors does not present a statistically significant (at a 95% confidence level) effect on the Mn initial leaching rate. These observations suggest that the oxidation effects of the acid concentration and the anodic electrochemical treatment help to initially release Mn from the foil's structure. The fact that the effect of the electrochemical treatment factor on the initial Mn leaching rate is different from its effect on the final leaching yield, suggests that Mn's leaching mechanism may change during the process [48].

3.4.3. Mn final extraction yield

The electrochemical treatment, the acid concentration and their interaction have a statistically significant (at a 95% confidence level) effect on the Mn final extraction yield (Fig. 8.a., Table 9). Firstly, a high acid concentration results in a greater Mn final extraction yield (Fig. 8.c.), as for the other metals studied in this work. Secondly, the cathodic

treatment leads to a greater Mn final extraction yield (Fig. 8.c.). Finally, the combination of high acid concentration (H₂SO₄ 2 M) and the cathodic treatment results in the highest Mn final extraction yield (Fig. 8.d.). This observation is consistent with the leaching reaction of transition metals in the cathodic sheet (see Section 3.6) and the fact that during the cathodic treatment, Mn(IV) is reduced to Mn(II), improving its leaching [25,26].

3.5. Recovery of the Al foil

In all the experiments performed with an electrochemical treatment (cathodic or anodic), the Al sheet was completely exfoliated, regardless of the acid concentration (Fig. S9). During the anodic treatment, oxygen is formed on the electrode; whereas during the cathodic treatment, hydrogen is formed on it. At the currents used in this work, the oxygen (or hydrogen) evolution reactions generate large amounts of gas bubbles in the tiny gap between the electrode and the foil interface, which can destabilize the Ni-Co-Mn structure, as well as the binder's interface. This destabilization reduces the adhesion of the active materials to the Al foil, causing the complete separation of the Al foil from the rest of the cathode and metal oxides [46]. Another possible cause of the Al foil peeling off may be the binder degradation by the strong oxidants produced at the electrodes [46]. In the case of anodic leaching, the Al foil is oxidized to Al₂O₃ whose adhesion is lower than the original Al sheet,

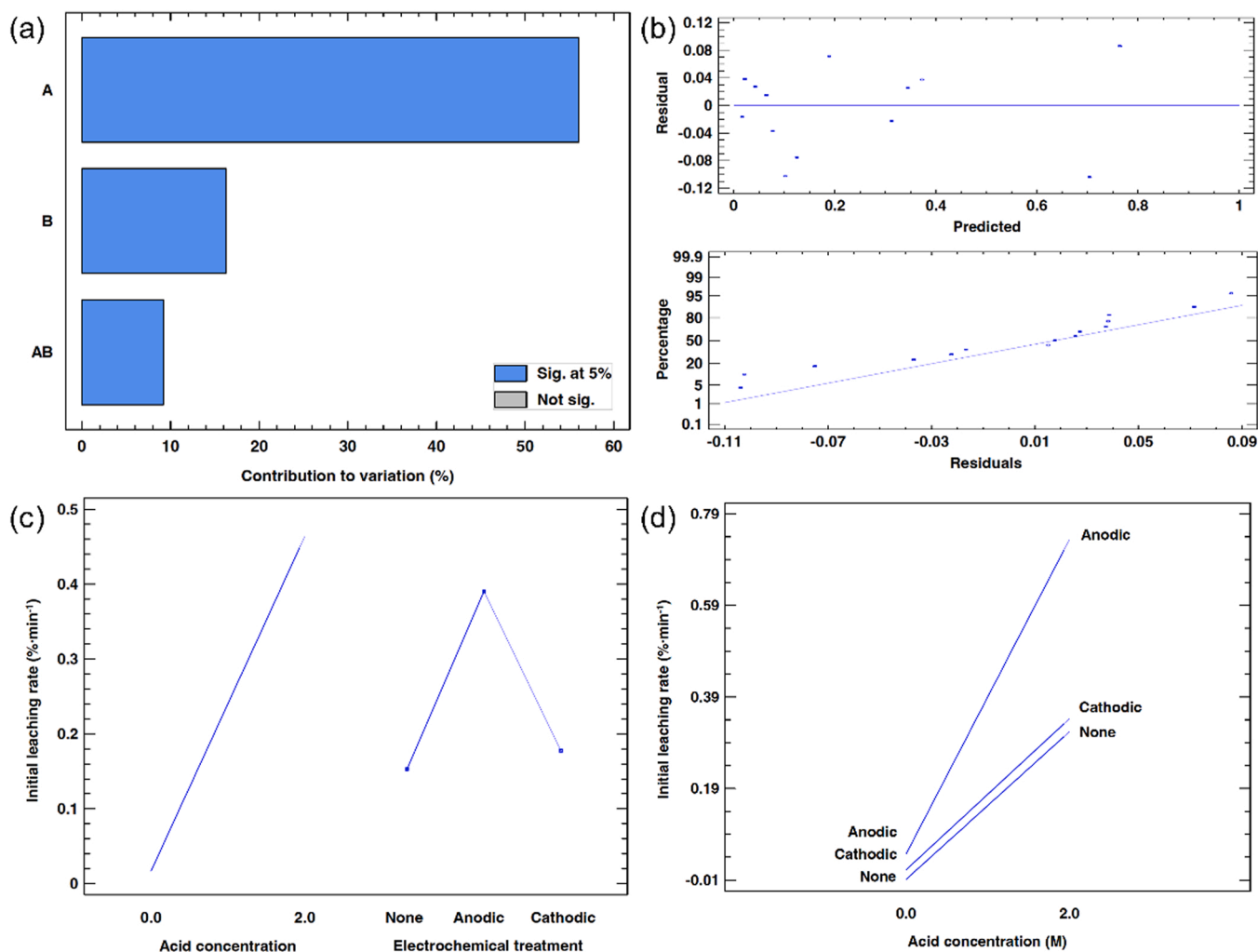


Fig. 5. Statistical analysis of the effect of the acid concentration (Factor A) and the electrochemical treatment (Factor B) on the Ni initial leaching rate. (a) Pareto chart, (b) validation plots (residual versus predicted plot, and normal probability plot of the residuals), (c) main effects plot, and (d) interaction plot. Study validated by (b) as the residuals are distributed without defined structure and with a linear pattern at the normal probability plot.

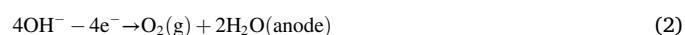
promoting its separation [45,47]. The separation of the Al foil allows the simultaneous recovery of three fractions in one step: the first fraction, the Al detached as a foil; the second fraction, the delaminated cathodic sheet which consists mainly of graphite; and the third fraction, the metals leached into the solution.

3.6. Discussion

The initial leaching rate of all elements is significantly speeded up by high acid concentrations. However, the best electrochemical treatment differs from one element to another. Co presents a higher initial leaching rate with a cathodic treatment, in line with its final extraction yield. Ni and Mn have a higher initial leaching rate with an anodic treatment, and Li with no electrochemical treatment (chemical leaching). From the final extraction yield perspective, Li's final yield is maximized when an anodic electrochemical treatment is used with a neutral electrolyte (i.e. Na₂SO₄); whereas in the Co, Ni and Mn cases, the final extraction yields are maximized when a cathodic electrochemical treatment is applied using a concentrated acidic electrolyte (2 M H₂SO₄).

The conditions that maximize the initial leaching rate are different from the conditions that maximize the final extraction yield, for all the elements (Table 10). This observation suggests that a change in the kinetics of the leaching process occurs during the experiments, which has already been hypothesized in literature [47]. The change in the kinetics

of the leaching process may be due to the destabilization of the structure of the cathodic material during the leaching process. In the case of Lithium, the anodic electrolytic treatment promotes delithiation by an excess of positive charge at the interface, as suggested by Thackeray's mechanism, [47] according to which Li is released into the solution in a process similar to the charging process of a Li-ion battery. The excess of positive charge causes Li migration from the anode to the cathode resulting in a concentration gradient that accelerates the dissolution of Li in the electrolyte [42]. The generation of OH⁻ ions in the cathode during the anodic leaching, causes the pH to raise to a pH of 10.5 within 10 min. At this pH, hydroxides of transition metal ions precipitate and therefore do not leach into the solution. This hypothesis is confirmed by the fact that no traces of Co and Mn, and only very low amounts of Ni (<5%), were detected in the final sample (i.e. t = 4 h) of the experiment corresponding to the anodic treatment with Na₂SO₄. The small presence of Ni is explained by the change in the layered structure of the battery's cathodic foil, which is destabilized by Li leaching, since Li is not replenished during the electrolysis. This destabilization results in a small presence of Nickel in the solution [47]. This observation opens a route for the selective leaching of Li. The reactions that take place during the anodic leaching in neutral media, based on [47], are:



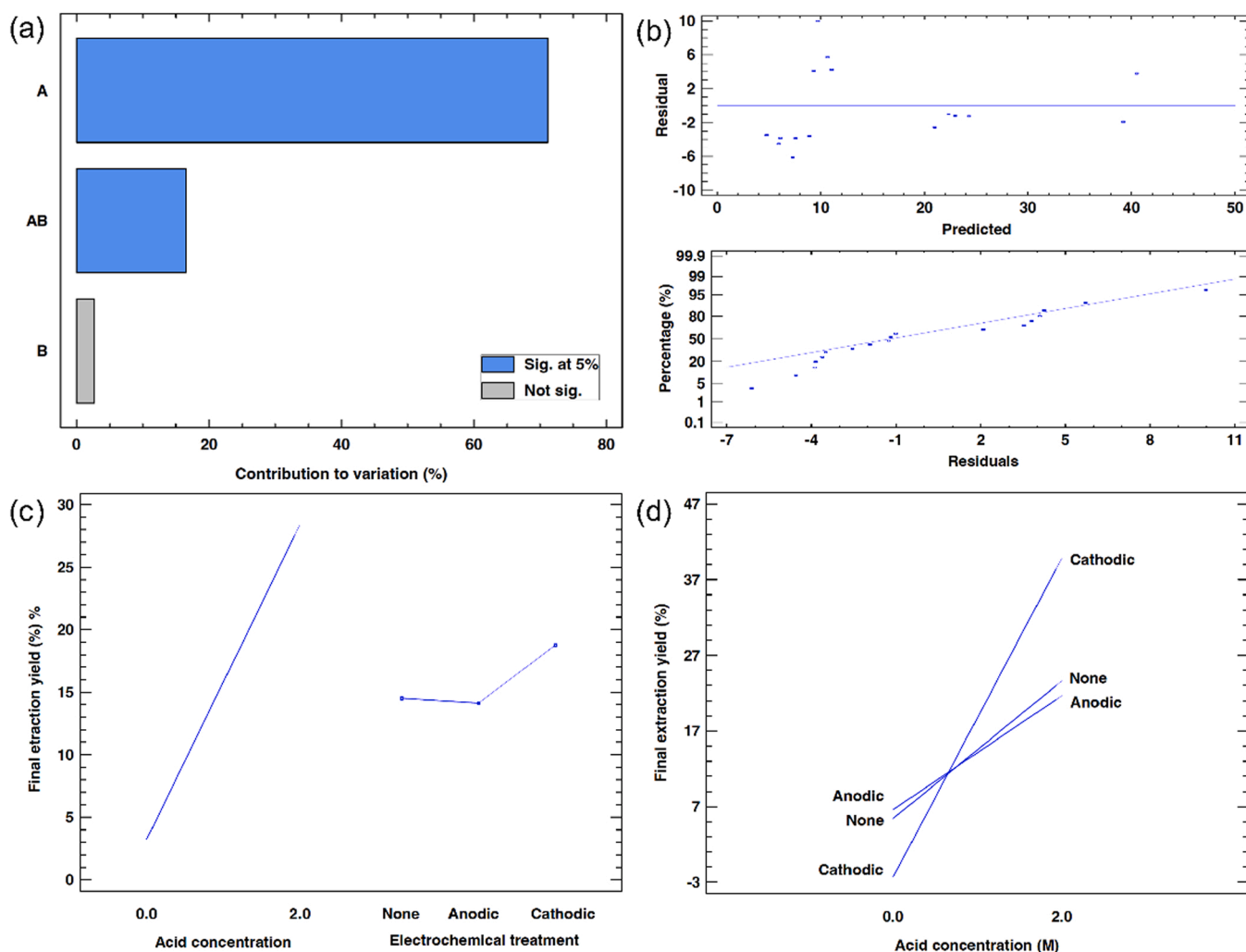
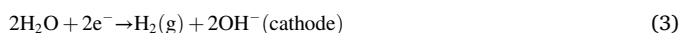
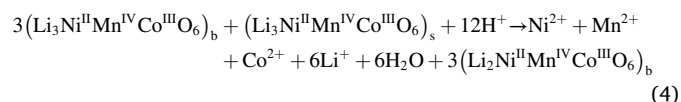


Fig. 6. Statistical analysis of the effect of the acid concentration (Factor A) and the electrochemical treatment (Factor B) on the Ni final extraction yield. (a) Pareto chart, (b) validation plots (residual versus predicted plot, and normal probability plot of the residuals), (c) main effects plot, and (d) interaction plot. Study validated by (b) as the residuals are distributed without defined structure and with a linear pattern at the normal probability plot.



The increase in acid concentration, with no electrochemical treatment, increases the final extraction yield for transition metals as the acid helps to destroy the molecular structure of the cathodic foil of the NMC battery, unstabilizing the layered structure and releasing the metals [42]. Therefore, in the case of Ni, Co and Mn, a highly acidic media is necessary to obtain a high final leaching yield. Protonation of the surface by acid-base reactions also involves a charge compensation by cationic and anionic redox reactions. During acid delithiation, the transition metals compensate the chemical deintercalation of Li. In addition, the reaction of the oxygen inside the material, also released from the structure, induces the formation of defects and macro-cracks. This allows the intercalation of the acid solution inside the layered structure, destabilizing the transition metals, and favoring the leaching process [48]. The dissolution reaction and the deintercalation in acidic media can be represented as follows, where subscript *s* refers to the surface of the particles in the cathodic foils and *b* refers to the bulk of these particles [48]:



In the case of Co and Mn, strong reducing conditions improve largely

their final leaching yield. The electrons supplied by the DC source reduce Mn(IV) and Co(III) in the solid phase to Mn(II) and Co(II), respectively. These reduced species leach easily into the solution. On the contrary, the overall valence of Ni (i.e. II) remains as in the original NMC oxide during the leaching process [49].

3.7. Optimized recycling strategy

Based on the optimum conditions for maximizing the final leaching yield of each element (Table 10), a novel and sustainable process can be proposed (Fig. 9) to selectively recover the different elements. The process, to be scientifically proved in further works, involves 3 sequential steps: first, an anodic treatment using a Na_2SO_4 electrolyte; second, a cathodic treatment in a mild acidic electrolyte; and finally, an electrochemical deposition. In the first step, the anodic treatment using a neutral Na_2SO_4 electrolyte achieves the selective dissolution of Li and the separation of the Al foil, in a single step. In the second step, the cathodic sheet (without the Al foil) is introduced into a mild acidic solution for extracting the transition metals (Ni, Mn and Co) via reductive leaching, using a cathodic leaching treatment, with no use of extra chemical reagents. Finally, in the last step, using an electrodeposition treatment, Ni and Co could be recovered on the cathode, where they codeposit as an alloy; whereas Mn is recovered on the anode, where it is deposited as Mn oxide.

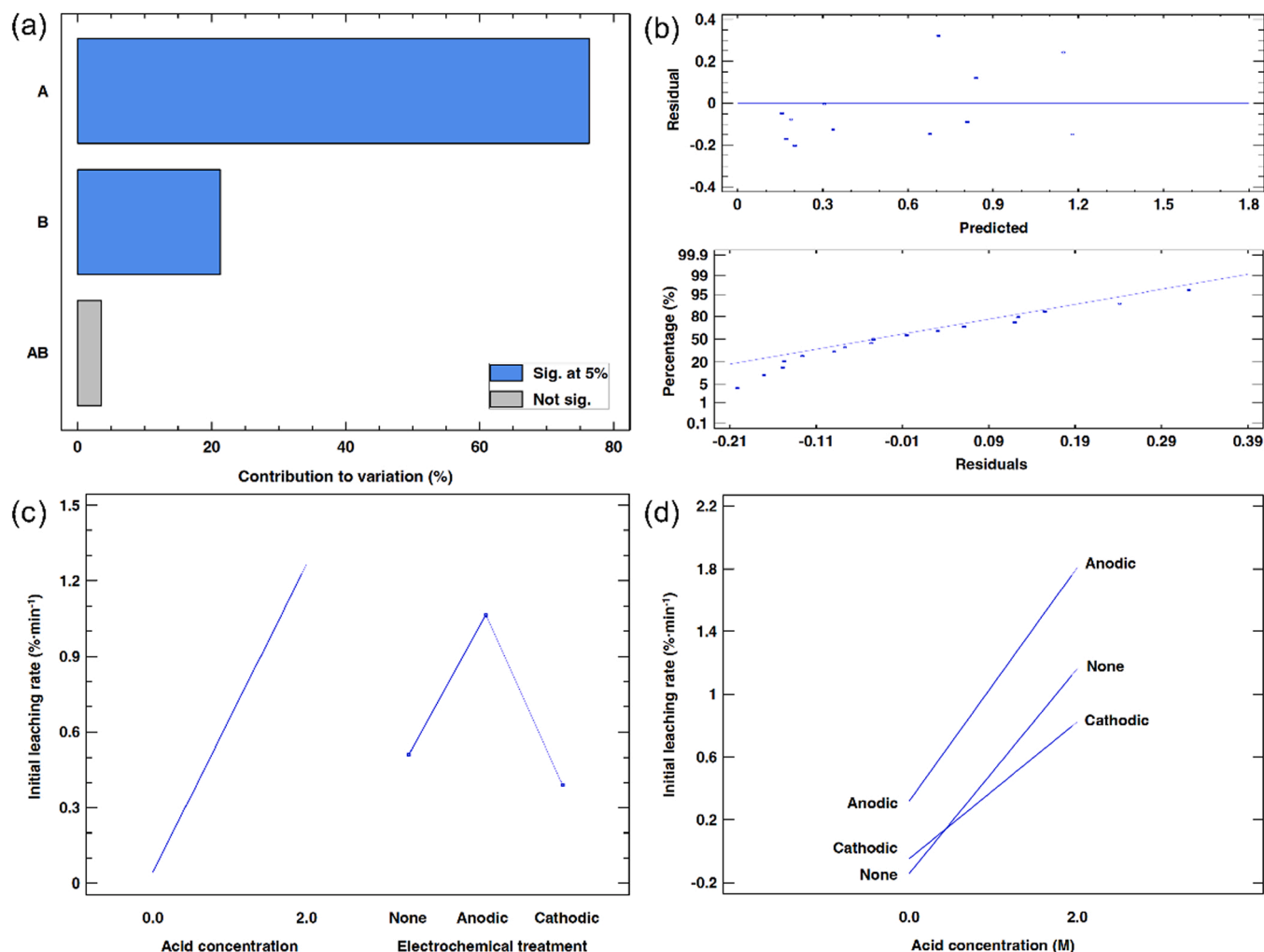


Fig. 7. Statistical analysis of the effect of the acid concentration (Factor A) and the electrochemical treatment (Factor B) on the Mn initial leaching rate. (a) Pareto chart, (b) validation plots (residual versus predicted plot, and normal probability plot of the residuals), (c) main effects plot, and (d) interaction plot. Study validated by (b) as the residuals are distributed without defined structure and with a linear pattern at the normal probability plot.

In this work, the achieved recoveries of the metals considering the best conditions of ANOVA results (Table 10) in 4 h, ambient temperature and voltages between 2 and 10 V were: > 90%, 55%, 35% and 40% for Li, Ni, Mn and Co, respectively. Al foil was 100% recovered after the electrochemical leaching. The results obtained in this work are different from those found in literature, summarized in Table 11, as the following process conditions differ from this study: the cathodic foil here is not thermal or chemically pre-treated, Al foil is included in the treatment, leaching yields are obtained at room temperature, employed voltages for the cathodic treatments and current densities are not declared. Electrochemical leaching was performed at galvanostatic mode (0.5 A) at room temperature and lower voltages compared to other methods available in literature (2–15 V). Consequently, the recycling process proposed above can be performed without any kind of pre-treatment, at room temperature, with neutral and mild acidic media, without any reducing chemicals (the reduction is achieved with the input of electrons by the DC source during the electrochemical treatment), and with relatively low voltages. All these advantages make the proposed process a green and environmentally friendly process for the recovery of the Al foil and the cathodic metals (Li, Co, Mn and Ni) of the battery cathodes.

As the main advantages of this process, it is worth noting the lack of pre-treatments, room temperature, neutral and mild acidic media, the reductive electrochemical leaching using electron as reductant, and low voltages. These advantages are key for this process to be considered

green and environmentally friendly for the recovery of the Al foil and the cathodic materials.

4. Conclusions

In this work, the effect of acid concentration and electrochemical treatment on the leaching of the different metals of a NMC cathode of a Li-ion EV battery was studied through a statistical analysis performed using a 3² factorial experimental design. Higher acid concentrations improve the leaching process for all the metals while the electrochemical treatment, anodic or cathodic, also has a significant effect albeit with a different effect on each one. Furthermore, a significant interaction exists between the levels of acid concentration and the type of electrochemical treatment. The different effect of both factors on the leaching of the different metals could be used strategically for a practical selective recovery of the cathodic materials. Lithium can be selectively leached in neutral media by using an anodic electrochemical treatment. Ni, Co, and Mn can be leached in a mildly acidic media by a cathodic electrochemical treatment, with no need of chemical reducing agents. Based on these results, a green process for recycling the cathodes of spent LIBs was proposed, that will be evaluated in further studies. This 3-sequential-step process would allow to recover separately the Al foil, the Li fraction, the Mn fraction, and the Ni-Co fractions (as an alloy). The main advantage of the proposed process is that it could be performed

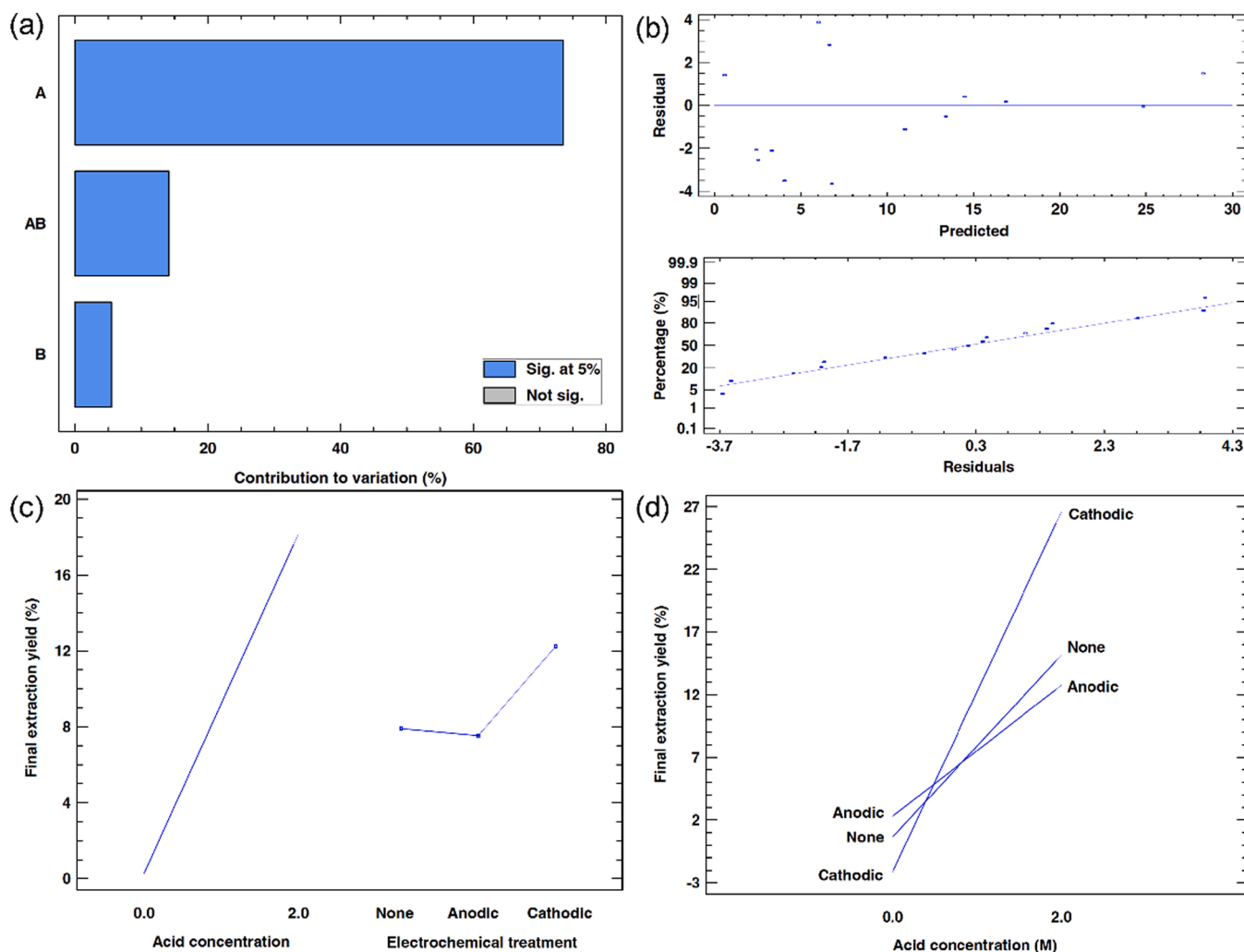


Fig. 8. Statistical analysis of the effect of the acid concentration (Factor A) and the electrochemical treatment (Factor B) on the Mn final extraction yield. (a) Pareto chart, (b) validation plots (residual versus predicted plot, and normal probability plot of the residuals), (c) main effects plot, and (d) interaction plot. Study validated by (b) as the residuals are distributed without defined structure and with a linear pattern at the normal probability plot.

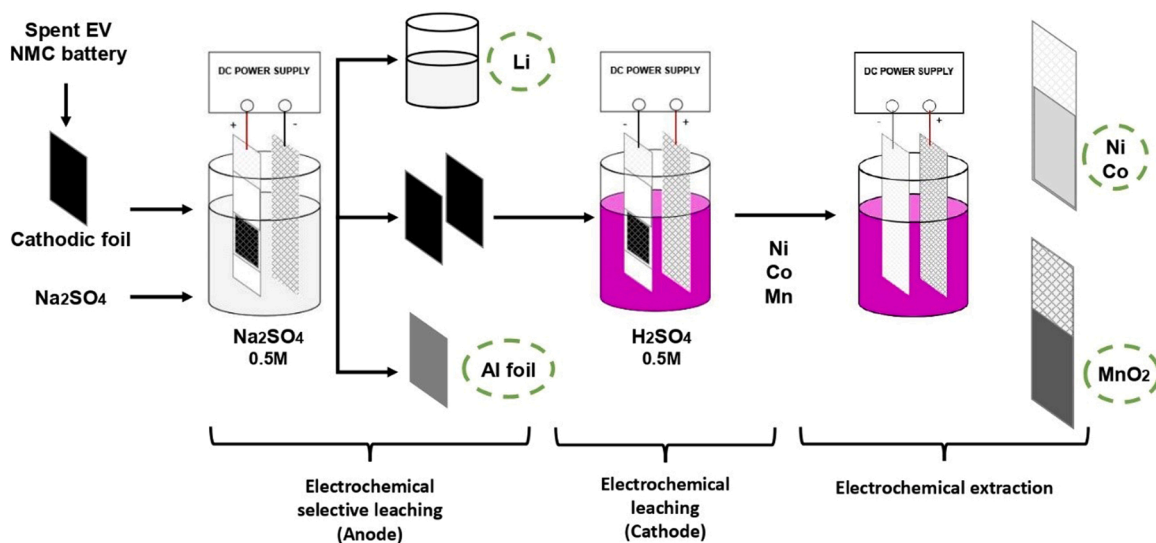


Fig. 9. Proposed optimized recycling process. The process consists in 3 steps: first, an anodic treatment using a Na₂SO₄ electrolyte; second, a cathodic treatment in a mild acidic electrolyte; and finally, an electrochemical deposition. The process would allow to recover separately 4 fractions: the Al foil, Li, Mn and Ni-Co. The main advantage of this process is that it is entirely ran at room temperature.

Table 11

Recovery yields and conditions for electrochemical recoveries reported in the literature.

Cathode	Temp. (°C)	Leaching agent	Yield	Conditions	Ref.
LiCoO ₂	70 °C	2.5 M DL-malic acid	97% Li 96% Co	8 V, 120 min at cathodic configuration. There is no comparison with anodic treatment or chemical leaching.	[41]
LiCoO ₂	70°C	1.5 M DL-malic acid	94% Li 90% Co	Al first dissolved in NaOH. Cathode calcined at 650 °C for 3 h. Powder was ground and extruded to be used only as cathode. Reaction time: 180 min.	[42]
NMC	1st step 50 °C. 2nd step 60 °C	Electrolysis of Na ₂ SO ₄ to NaOH and H ₂ SO ₄	> 99% Li, Ni, Mn, Co	Al dissolved with electro generated NaOH and precipitated. 2nd step: Cathode is leached with the electro generated H ₂ SO ₄ 1 M and 2% H ₂ O ₂ as reducing agent.	[43]
NMC	25 °C	Acidic 2,5 g/L(NH ₄) ₂ SO ₄	> 98% Li	Material was immersed in dimethyl carbonate. Anodic leaching at 25 V, 80°C and 3 h needed for a complete leaching of Li. Mn and Co were directly used from the leaching residue to resynthesize cathodic materials.	[44]
NMC	60 °C	1.5 M DL-malic acid	> 99% for Li, Ni, Mn, Co	Al is dissolved in NaOH. Cathode is calcined at 650 °C for 4 h. Powder was ground and extruded and set as the cathode of the electrochemical cell at 8 V. There is no anodic or chemical comparison.	[45]

without any kind of chemical or thermal pre-treatments, at room temperature, with neutral and mild acidic media, without any reducing chemicals, and with relatively low voltages, which would make it a green and environmentally friendly process.

CRedit authorship contribution statement

Laura Grima-Carmena: Conceptualization, Investigation, Methodology, Data curation, Formal analysis, Writing – original draft, Visualization, Writing – review & editing. **Silvia Oyonarte-Andrés,** Conceptualization, Methodology, Investigation, Data curation, Project administration, Funding acquisition. **Juan José Giner-Sanz:** Conceptualization, Methodology, Validation, Software, Data curation, Formal analysis, Writing – original draft, Visualization, Writing – review & editing. **Montserrat García-Gabaldón:** Supervision, Writing – review & editing. **Francisco Bosch-Mossi:** Resources, Supervision, Funding acquisition, Project administration, Writing – review & editing. **Valentín Pérez-Herranz:** Supervision, Writing – review & editing.

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.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2023.110423](https://doi.org/10.1016/j.jece.2023.110423).

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