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Original

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Review

Analysis of Lanthanum and Cobalt Leaching Aimed at Effective Recycling Strategies of Solid Oxide Cells

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Abstract: Lanthanum and cobalt are Critical Raw Materials and components of Solid Oxide Cells—SOCs electrodes. This review analyses lanthanum and cobalt leaching from waste materials (e-waste, batteries, spent catalysts), aiming to provide a starting point for SOC recycling, not yet investigated. The literature was surveyed with a specific interest for leaching, the first phase of hydrometallurgy recycling. Most references (86%) were published after 2012, with an interest higher (85%) for cobalt. Inorganic acids were the prevailing (>80%) leaching agents, particularly for lanthanum, while leaching processes using organic acids mostly involved cobalt. The experimental conditions adopted more diluted organic acids (median 0.55 M for lanthanum and 1.4 M for cobalt) compared to inorganic acids (median value 2 M for both metals). Organic acids required a higher solid to liquid ratio (200 g/L), compared to inorganic ones (100 g/L) to solubilize lanthanum, while the opposite happened for cobalt (20 vs. 50 g/L). The process temperature didn't change considerably with the solvent (45–75 °C for lanthanum, and 75–88 °C for cobalt). The contact time was higher for lanthanum than for cobalt (median 3–4 h vs. 75–85 min). Specific recycling processes are crucial to support SOC's value chain in Europe, and this review can help define the existing challenges and future perspectives.

Keywords: circular economy; critical raw material; green chemistry; leaching; SOC



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1. Introduction

With the ever-rising demand for energy, in recent years the interest in research towards alternative solutions to conventional power generation systems has grown [1,2]. Thanks to their high electrical efficiency, low noise and low emissions of pollutants, Fuel Cells (FCs) are expected to play a crucial role in achieving the European Commission (EC) goal of carbon neutrality by 2050, contributing to the reduction of Greenhouse Gases (GHG) emissions [2,3]. Compared with other FCs, solid oxide fuel cells (SOFCs) displayed 60–80% higher conversion efficiency and longer durability [4]. SOFCs and solid oxide electrolyser cells (SOECs) are jointly referred to as solid oxide cells (SOCs). SOFCs offer an efficient alternative to combustion technology for electricity production, while SOECs offer enhanced efficiency in the conversion of steam to hydrogen [5]. Thanks to their outstanding properties, SOFCs are excellent candidates for distributed stationary power generation: the global SOFCs market size is expected to grow from 1.09 billion USD in 2021 to 5.31 billion USD in 2028 [3,6]. Accordingly, high amounts of waste SOC's will be generated in the next few years, and a related efficient end-of-life (EoL) management strategy still does not exist [1,2].

The components of a SOC mainly consist of porous layers (a cathode and an anode) separated by a dense electrolyte layer [7] containing metals (such as nickel and copper in the fuel electrode and cobalt and strontium in the oxygen electrode), rare-earth elements (REEs) as yttrium and cerium in both fuel electrode and electrolyte and lanthanum in the oxygen electrode.

Considering the economic importance of these elements and the risk related to their supply for the European Union (EU), REEs and cobalt were included in the list of Critical Raw Materials (CRMs) in 2020 [8]. Therefore, the development of an efficient strategy for the recovery of CRMs and valuable metals from waste SOC would provide an alternative to the consumption of virgin raw materials, reducing the costs and the environmental impact of their productive process [2,3] and supporting FCs value chain in EU [8]. In the past 10 years, extensive research has been carried out to develop techniques aimed at the recovery of REEs and valuable metals from various EoL materials such as e-waste, spent catalysts and batteries [9–12]. Different approaches have been proposed: pyrometallurgy and hydrometallurgy at full-scale and precipitation, filtration, liquid–liquid solvent extraction and bioleaching at a smaller scale. Pyrometallurgical processes are based on the thermal decomposition of the non-metallic components, and the recovered metals are converted into alloys [9]. Hydrometallurgical processes involve several phases in sequence [10]: leaching (through an acidic/alkali/organic solvent), recovery of the target compound (through precipitation or solvent extraction) as “precursor” and conversion into the active recycled material. Sustainable hydrometallurgical processes (e.g., using mild solvents, limiting the energy demand and emissions) seem to be the most promising solution, compared to the pyrometallurgical approach [10,11], also assuring a high recovery efficiency for more elements. However, what is intended for the “sustainable” (or “green”) process has not been specifically defined.

Lanthanum is a light REE, an expensive metal and a CRM [8] with many applications in automobile catalytic converters, ceramics, fluid catalytic cracking, glass additives, battery alloys, phosphor and glass polishing industries. The increasing interest in these fields has recently led to important growth in both the demand and price of REEs. Cobalt is an essential metal in modern industry and a CRM [8,11–13] widely employed in the electronic field (25% of the globally produced cobalt is employed in rechargeable lithium-ion batteries for mobile devices), the aerospace and automotive industries and in many other fields (metallurgy and industrial processes aimed at producing textiles, glass and ceramics, pharmaceuticals and chemicals) [8,14,15].

To the best of our knowledge, despite the urgent need for valid recycling technologies for EoL SOC, nowadays, the number of studies investigating this topic is extremely low. The only papers exploring the recovery of valuable elements from waste cells are focused on types different from SOC [1,16,17]. On the other hand, many literature studies proposed successful processes for lanthanum and cobalt recovery from other waste materials [9–12]. With the aim to explore the actual perspectives for efficient recovery of lanthanum and cobalt from EoL SOC, this review analyzed the current scientific literature related to the leaching (i.e., the first phase of a hydrometallurgical recycling process) of these two metals from different sources (as waste batteries, e-waste and spent catalysts). Lanthanum and cobalt are commonly both present in the perovskite structure of SOC oxygen electrodes [7]; therefore, it is essential to identify an efficient process specifically adapted to recover both elements from a single material. In addition, the adherence of the different leaching processes reported by literature to the Green Chemistry principles [18] was evaluated with the aim of selecting the “green” processes.

2. Materials and Methods

The selection and classification of the scientific literature on lanthanum and cobalt leaching from waste materials was carried out according to the following three phases:

- (a) Literature survey and selection: firstly, the scientific literature was surveyed running a comprehensive search on Scopus, Science Direct and Web of Science databases.

The adopted keywords were 'lanthanum' AND 'cobalt' AND 'leaching' AND 'hydrometallurgical' AND 'recovery' AND 'waste'. Secondly, a screening of the results based on the publication language and type of reference was made, selecting only research papers and reviews in English. Thirdly, a chronological filter was applied to exclude the references published before 2000. The abstracts of the resulting papers were analyzed to understand whether they fall under the scope of this study. More studies, compliant with the above-mentioned criteria, were added from the references cited by the selected review papers.

- (b) Literature classification: the articles selected in the previous phase were classified according to the type of metal they focus on. Another classification was made considering the type of solvent used for the leaching process, with a further distinction based on its nature (inorganic or organic).
- (c) Evaluation of the process approach: after the literature selection, it was observed that the word "green" was present in the title, abstract or among the keywords, despite being not strictly connected to the aim of the research. In many other papers, the word "green" and expressions like "environmentally friendly" and "sustainable" (referred to as the processes) occurred in the text. However, the criteria that lead to define a process "green" were not specified. To provide a clear and unambiguous classification, in this review, a process is classified "green" if it is compliant with at least three principles of Green Chemistry [18].

To make a comparison of the leaching agents employed in the scientific papers selected for this review, the adherence of the different solvents to the Green Chemistry principles has been evaluated. Among the twelve principles, only the following five (No. 3, 4, 5, 10, and 12) were considered, being the most involved in the processes for the recovery of lanthanum and cobalt:

- 3. Less Hazardous Chemical Syntheses: the toxicity to human health and the environment was evaluated by consulting the safety data sheet of each solvent.
- 4. Designing Safer Chemicals: to evaluate the safety of a chemical agent, its concentration was evaluated. First, considering all the references, the overall median value of the concentration of the bleaching agent was determined. The overall median value was then compared to the specific median value calculated for each solvent. If the specific median concentration was lower or equal to the overall median value, the solvent was considered a safer chemical.
- 5. Safer Solvents and Auxiliaries: a solvent was considered compliant with this principle if in at least 60% of the processes proposed by the selected references it was used without the addition of an auxiliary agent.
- 10. Design for Degradation: the products obtained at the end of the leaching process were analyzed. In the case of inorganic solvents, the released products (NO_x , Cl_2 , or SO_3) and the leachate obtained were considered a threat to the environment.
- 12. Inherently Safer Chemistry for Accident Prevention: the potential for chemical accidents (releases, explosions, and fires) of all the solvents was evaluated from their safety data sheet.

Afterward, with the aim of defining the optimal conditions for lanthanum and cobalt leaching, box plots were built considering the values of the experimental parameters adopted in the selected studies. Some references proposed different operative conditions: in these cases, looking at the leaching efficiency of the various processes, only the procedures that were relevant to the scope of this review were considered. Then, the median value of each parameter was considered to obtain representative values of the operative conditions. Finally, with the purpose of estimating the experimental parameters for the leaching process of lanthanum and cobalt in a single process, the median value of the parameters of all the processes was calculated.

3. Results and Discussion

3.1. Literature Selection and Classification

Figure 1 shows the chronological distribution of 65 of the 70 scientific papers (five studies were excluded, not being unambiguously “green” or not) selected for this review according to the methodology described in Section 2. Only nine references were published between 2001 and 2011; most studies (86%) belong to the last decade, pointing out the growing interest in the subject. The peak was reached in 2017 (12 references out of a total of 65). The residual studies (35%) were published from 2018 to 2021.

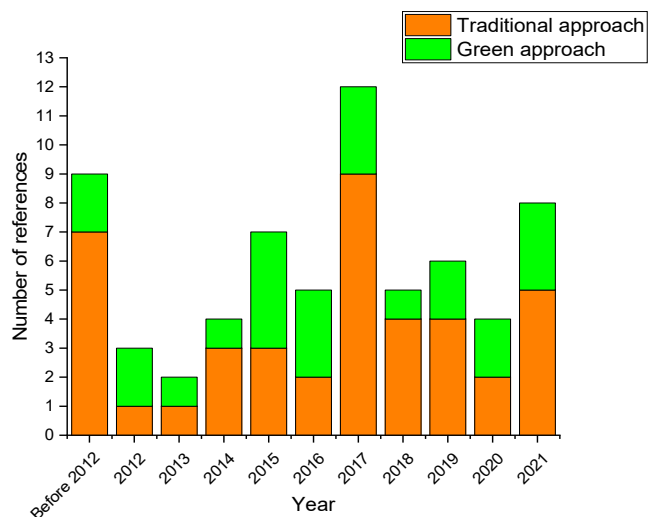


Figure 1. Chronological distribution of the scientific papers selected for this review.

Considering the leaching processes applied, the 65 references were further divided into two groups: those with a “traditional” approach to the leaching of lanthanum and cobalt and those with a “green” approach (e.g., compliant with at least 3 of the 12 principles of Green Chemistry, as defined in Section 2). Before 2015, no more than two articles per year explored cobalt and lanthanum leaching through a “green” process, while in 2015 and 2016 the trend has reversed (respectively 57% and the 60% of the studies considered a “green” process). Since 2017 the traditional approach has been prevalent.

Considering the contents of the 65 selected references, 43 were related to cobalt (66%), while 10 were focused on lanthanum (15%); the 12 residual references considered the leaching of both cobalt and lanthanum. Some references did not focus strictly on lanthanum, but in wider terms, they were related to REEs. The number of described processes dedicated to REEs (25, also considering the ones aimed at the leaching of both lanthanum and cobalt) was much lower compared to the ones considering cobalt (74). The 65 selected references have been further reduced to 59, eliminating the ones referred to bioleaching processes, and some reviews that did not clearly specify the experimental parameters. Within these 59 references, 88 processes were identified: the proposed operative conditions are reported in Table 1, where the field of application, the experimental parameters (type of solvent and concentration, reducing agent, solid to liquid ratio, temperature and contact time) and the recovery efficiency are detailed.

Considering the processes listed in Table 1, since 2017, the interest in the hydrometallurgical processes for REEs’ recovery has grown (Figure 2). Overall, the leaching agents were mostly acids (sulfuric, nitric, hydrochloric and citric) (>80%) but other types of solvents were also reported. Until 2012, sulfuric acid was the only lixiviant used for REEs’ leaching (Figure 2A); processes using nitric and hydrochloric acid were developed afterward. Regarding cobalt leaching (Figure 2B), organic acids were the most common solvents adopted in the last 10 years, followed by sulfuric and hydrochloric acids.

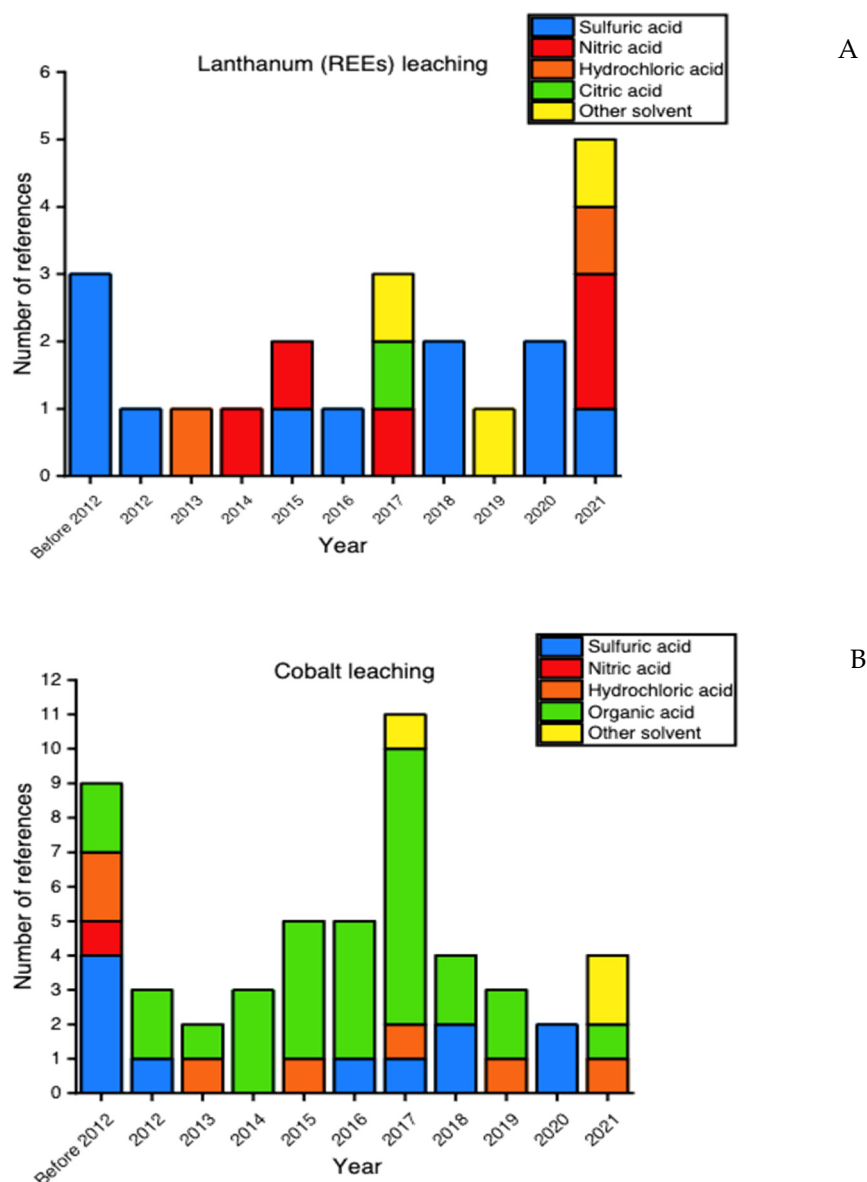


Figure 2. Type of solvents considered for (A) lanthanum and (B) cobalt leaching in the scientific papers selected for this review.

The columns in Table 2 show the different leaching agents that respect (green dot) or do not respect (red dot) the five considered Green Chemistry principles, as specified in Section 2. Even though sulfuric acid is not classified as toxic, according to the US Hazardous Materials Identification System (HIMS) its health hazard rate is 3 (the ratings range from 0 to 4). For this reason, sulfuric acid was considered non-compliant with the third Green Chemistry principle. It was found that all organic acids comply with more than three of the five principles considered. On the contrary, inorganic acids satisfy less than three of the principles: it was observed that in this class of lixivants, nitric acid is less compliant with the five considered Green Chemistry principles.

Table 1. List of the selected references describing the recovery of lanthanum and cobalt from various materials (M: mol/L; S/L: solid to liquid ratio).

| | Solvent (Concentration) | Reducing Agent | S/L (g/L) | T (°C) | Contact Time (h) | Recovery Efficiency % | Reference |
|---|--|--|-----------|-------------------------------------|-------------------------------------|--------------------------|-----------|
| Recovery of lanthanum | | | | | | | |
| Spent cracking catalyst | Nitric acid (7 M) | - | 100 | 90 | 3 | 99% La | [19] |
| Spent cracking catalyst | Nitric acid (5 M) | - | 10 | 80 | 3 | ≈100% La | [12] |
| Spent NiMH batteries | Nitric acid (4 M) | - | 83.3 | 70 | | ≈30% La | [20] |
| Cropland soil | Nitric acid (0.1 M) | - | 100 | 20 | 72 | 62.67% La | [21] |
| Spent catalyst | Citric acid (0.1 M) | - | 200 | 30 | 4 | 100% La | [22] |
| Spent catalyst | Citric acid (1 M) | - | 200 | 60 | 5 | 100% La | [22] |
| Spent catalyst | Citric acid (2 M) | - | 200 | 80 | 6 | 100% La | [22] |
| Cropland soil | Citric acid (0.1 M) | - | 100 | 20 | 72 | 66.59% La | [21] |
| Cropland soil | EDTA (0.1 M) | - | 100 | 20 | 72 | 79.6% La | [21] |
| Spent cracking catalyst | Sulfuric acid (2 M) | - | 150 | 25 | 3 | 61.2% La | [23] |
| Spent cracking catalyst | Sulfuric acid (2 M) | - | 150 | 80 | 3 | 89% La | [23] |
| Spent NiMH batteries | Sulfuric acid (2 M) | - | 100 | | 4 | 99.9% La | [24] |
| Spent NiMH batteries | First stage: Sulfuric acid (2 M) Second stage: H ₂ O | - | 96.2 | First stage: 30 Second stage: RT | First stage: 3 Second stage: 1.5 | 80.1% La | [25] |
| WEEE | Sulfuric acid (1 M) | - | 50 | 80 | 1 | 60% La | [9] |
| Recovery of lanthanum and cobalt | | | | | | | |
| Spent NiMH batteries | HCl (1 M) | - | 20 | 45 | 1 | 94.61% Co 99.14% La | [26] |
| Spent NiMH batteries | HCl (0.5 M) | - | 20 | 100 | 0.5 | 99.28% Co 97.02% La | [26] |
| Spent NiMH batteries | HCl (1 M) | - | 20 | 65 | 0.5 | 94.13% Co 95.57% La | [26] |
| Spent NiMH batteries | HCl (12 M) | - | 150 | 40 | 1.67 | | [27] |
| Spent NiMH batteries | Sulfuric acid (3 M) | - | 150 | First stage: 80 Second stage: RT | First stage: 3 Second stage: 1 | 99% La 76% Co | [28] |
| Spent NiMH batteries | Sulfuric acid (1 M) | - | 25 | 90 | 4 | ≈100% Co ≈90% La | [29] |
| Spent NiMH batteries | Sulfuric acid (3 M) | - | 100 | 25 | 1.25 | 88.7% La 79.4% Co | [30] |
| Spent NiMH batteries | Sulfuric acid (2 M) | - | 100 | 75 | 2 | 97.8% Co 69.5% La | [31] |
| Spent NiMH batteries | Sulfuric acid (2 M) | - | 50 | 90 | 4 | 92.31% Co 84% La | [32] |
| Spent NiMH batteries | Sulfuric acid (2 M) | - | 100 | 20 | 2 | 100% Co 0% La | [33] |
| Spent NiMH batteries | Sulfuric acid (3 M) | - | 133 | 95 | 4 | >90% Co <5% RE | [34] |
| Recovery of cobalt | | | | | | | |
| Spent lithium-ion batteries | HCl (4 M) | - | 100 | 80 | 1 | | [35] |
| Spent lithium-ion batteries | HCl (1 M) | - | 10 | RT | 2 | 90% Co | [36] |
| Spent NiMH batteries | HCl (8 M) | - | 510 | 30 | >0.5 | >90% Co | [37] |
| Spent lithium-ion batteries | HCl (2 M) | - | 25 | 60 | 5 | 77% Co | [38] |
| Spent lithium-ion batteries | HCl (4 M) | - | 20 | 80 | 1 | 99.5% Co | [39] |
| Spent lithium-ion batteries | HCl (5 M) | - | 10 | 95 | 1.17 | 99.74% Co | [40] |
| Lateritic chromite overburden | Oxalic acid (0.15 M) | - | 20 | 80 | 3 | 44.33% Co | [41] |
| Spent lithium-ion batteries | Oxalic acid (0.23 M) | H ₂ O ₂ (0.46 M) | 15 | 65 | 1 | | [42] |
| Spent lithium-ion batteries | Oxalic acid (0.46 M) | - | 15 | 90 | 1 | | [42] |
| Spent lithium-ion batteries | Oxalic acid (1 M) | - | 50 | 80 | 2 | 98% Co | [43] |
| Spent lithium-ion batteries | Oxalic acid (1 M) | - | 15 | 95 | 2.5 | 97% Co | [44] |

Table 1. Cont.

| | Solvent (Concentration) | Reducing Agent | S/L (g/L) | T (°C) | Contact Time (h) | Recovery Efficiency % | Reference |
|-----------------------------|-----------------------------|--|-----------|--------|---------------------|---|-----------|
| Spent lithium-ion batteries | Lactic acid (1.5 M) | H ₂ O ₂ (0.5 v%) | 20 | 70 | 0.33 | 98.9% Co | [45] |
| Spent lithium-ion batteries | Ascorbic acid (1.25 M) | Ascorbic acid (1.25 M) | 25 | 70 | 0.33 | 94.8% Co | [46] |
| Spent lithium-ion batteries | Succinic acid (1.5 M) | H ₂ O ₂ (4 v%) | 15 | 70 | 0.67 | 96% Co | [47] |
| Spent lithium-ion batteries | L-Aspartic acid (1.5 M) | H ₂ O ₂ (4 v%) | 10 | 90 | 2 | 60% Co | [48] |
| Spent lithium-ion batteries | Iminodiacetic acid (1 M) | Ascorbic acid (0.02 M) | 3 | 80 | 6 | 91% Co | [49] |
| Spent lithium-ion batteries | Maleic acid (1 M) | Ascorbic acid (0.02 M) | 4 | 80 | 6 | 97% Co | [49] |
| Spent lithium-ion batteries | Citric acid (2 M) | H ₂ O ₂ (1.25 v%) | 30 | 60 | 2 or 5 | 81.5% Co after 2 h 96.46% Co after 5 h | [50] |
| Spent lithium-ion batteries | Citric acid (1.25 M) | H ₂ O ₂ (1 v%) | 20 | 90 | 0.5 | 92% Co | [48] |
| Spent lithium-ion batteries | Citric acid (2 M) | H ₂ O ₂ (1.03 v%) | 30 | 80 | 2 | 84.04% Co | [50] |
| Spent lithium-ion batteries | Citric acid | H ₂ O ₂ (1 v%) | 15 | 90 | 5 | 99.07% | [51] |
| Spent lithium-ion batteries | Citric acid (1.5 M) | Tea waste (0.4 g/g) | 30 | 90 | 2 | 96% Co | [52] |
| Spent lithium-ion batteries | Citric acid (1.5 M) | Phytolacca Americana (0.4 g/g) | 40 | 80 | 2 | 83% Co | [52] |
| Spent lithium-ion batteries | Citric acid (2 M) | H ₂ O ₂ (0.6 g/g) | 50 | 70 | 1.33 | 98% Co | [52] |
| Spent lithium-ion batteries | Citric acid (1.25 M) | H ₂ O ₂ (1 v%) | 20 | 90 | 0.5 | 90% Co | [53] |
| Spent lithium-ion batteries | Citric acid (1.25 M) | H ₂ O ₂ (1 v%) | 16.7 | 90 | 0.58 | 90.2% Co | [54] |
| Spent lithium-ion batteries | Citric acid (2 M) | H ₂ O ₂ (0.55 M) | 25 | 60 | 5 | 96% Co | [38] |
| Spent lithium-ion batteries | Citric acid (2 M) | H ₂ O ₂ (3 v%) | 20 | 80 | 1.5 | | [55] |
| Spent lithium-ion batteries | Citric acid (0.1 M) | Ascorbic acid (0.02 M) | 5 | 80 | 6 | 80% Co | [56] |
| Spent lithium-ion batteries | Citric acid (2 M) | H ₂ O ₂ (2 v%) | 33.3 | 80 | 1.5 | 95% Co | [57] |
| Spent lithium-ion batteries | Citric acid (2.5 M) | H ₂ O ₂ (5 v%) | 25 | 85 | 2 | 85.1% Co | [58] |
| Spent lithium-ion batteries | Citric acid (1.25 M) | - | 20 | 80 | 2 | 62% Co | [59] |
| Spent lithium-ion batteries | Citric acid (1.25 M) | H ₂ O ₂ (2 v%) | 20 | 80 | 0.33 | 74% Co | [59] |
| Spent lithium-ion batteries | Citric acid (1.25 M) | H ₂ O ₂ (2 v%) | 20 | 95 | 0.5 | 91% Co | [59] |
| Spent lithium-ion batteries | Citric acid (1.5 M) | H ₂ O ₂ (2 v%) | 20 | 95 | 0.5 | 95% Co | [59] |
| Spent lithium-ion batteries | Citric acid (1 M) | - | 20 | 95 | 1.5 | 95% Co | [59] |
| Spent lithium-ion batteries | Sulfuric acid (1 M) | H ₂ O ₂ (4 v%) | 20 | 95 | 1 | 85.4% Co | [60] |
| Spent NiMH batteries | Sulfuric acid (2 M) | - | 100 | 20 | 1.17 | 100% Co | [61] |
| Spent lithium-ion batteries | Sulfuric acid (2 M) | H ₂ O ₂ (0.55 M) | 25 | 40 | 5 | 48% Co | [38] |
| Spent lithium-ion batteries | Sulfuric acid (2.5 M) | H ₂ O ₂ (5 v%) | 25 | 85 | 3 | 82.9% Co | [62] |
| Spent lithium-ion batteries | Sulfuric acid (2 M) | H ₂ O ₂ (2 v%) | 100 | 70 | 5 | 96.7% Co | [62] |
| Spent lithium-ion batteries | Sulfuric acid (2 M) | D-glucose (12% g/g scraps) | 100 | 80 | 5 | 93.1% Co | [62] |
| Spent lithium-ion batteries | Sulfuric acid (2 M) | Ascorbic acid (10% g/g scraps) | 100 | 80 | 5 | 100.7% Co | [62] |
| Spent lithium-ion batteries | Sulfuric acid (2 M) | H ₂ O ₂ (10 v%) | 33.3 | 70 | 2 | 98.46% | [63] |
| Spent lithium-ion batteries | Sulfuric acid (1 M) | NaHSO ₃ (0.075 M) | 20 | 95 | 4 | 91.6% Co | [64] |
| Spent lithium-ion batteries | DL-Malic acid (1.5 M) | H ₂ O ₂ (2 v%) | 20 | 90 | 0.67 | 93% Co | [48] |
| Spent lithium-ion batteries | DL-Malic acid (2 M) | H ₂ O ₂ (2 v%) | 30 | 80 | 2 | 84.02% Co | [50] |
| Spent lithium-ion batteries | DL-Malic acid (1.25 M) | H ₂ O ₂ (2 v%) | 20 | 95 | 0.33 | 91% Co | [59] |

Table 1. Cont.

| | Solvent (Concentration) | Reducing Agent | S/L (g/L) | T (°C) | Contact Time (h) | Recovery Efficiency % | Reference |
|-----------------------------|------------------------------|--|-----------|--------|---------------------|--------------------------|-----------|
| Spent lithium-ion batteries | DL-Malic acid (1.5 M) | H ₂ O ₂ (2 v%) | 20 | 90 | 0.33 | 73% Co | [59] |
| Spent lithium-ion batteries | DL-Malic acid (1 M) | H ₂ O ₂ (2 v%) | 20 | 95 | 0.5 | 98% Co | [59] |
| Spent lithium-ion batteries | DL-Malic acid (1.5 M) | H ₂ O ₂ (2 v%) | 20 | 95 | 0.5 | 98% Co | [59] |
| Spent lithium-ion batteries | DL-Malic acid (1.5 M) | H ₂ O ₂ (2 v%) | 20 | 90 | 0.67 | 93% Co | [65] |
| Spent lithium-ion batteries | L-tartaric acid (2 M) | H ₂ O ₂ (4 v%) | 17 | 70 | 0.5 | 98.64% | [66] |
| Spent lithium-ion batteries | Tartaric acid (0.4 M) | Ascorbic acid (0.02 M) | 2 | 80 | 5 | >95% Co | [67] |
| Spent lithium-ion batteries | Tartaric acid (1 M) | Glucose (20 g/L) | 10 | 80 | 1.5 | 46.6% Co | [68] |
| Spent lithium-ion batteries | Tartaric acid (1 M) | Ascorbic acid (30 g/L) | 10 | 80 | 1.5 | 47.3% Co | [68] |
| Spent lithium-ion batteries | Tartaric acid (1 M) | H ₂ O ₂ (10 v%) | 10 | 80 | 1.5 | 53.2% Co | [68] |
| Spent lithium-ion batteries | Tartaric acid (0.6 M) | H ₂ O ₂ (3 v%) | 33.3 | 80 | 0.5 | 97% Co | [69] |
| Spent lithium-ion batteries | Formic acid (2 M) | H ₂ O ₂ (6 v%) | 50 | 60 | 0.19 | 90.49% Co | [70] |
| Spent lithium-ion batteries | Acetic acid (3.5 M) | H ₂ O ₂ (4 v%) | 40 | 60 | 1 | 93.62% Co | [71] |
| Spent lithium-ion batteries | Nitric acid (1 M) | H ₂ O ₂ (1.7 v%) | 20 | 75 | 0.5 | >95% Co | [72] |
| Spent lithium-ion batteries | Phosphoric acid (2 M) | H ₂ O ₂ (2 v%) | 8 | 90 | 1 | 99% Co | [73] |
| Spent lithium-ion batteries | Hydrogen fluoride (15 v%) | - | 20 | 75 | 2 | 58% Co | [74] |

Table 2. Evaluation of the compliance of the acid leaching agents to the five considered Green Chemistry principles (green: compliant; red: not compliant).

| No. Green Chemistry Principle | Leaching Acid Agent | | | | | |
|--|---------------------|--------------|----------|--------|----------|--------|
| | Nitric | Hydrochloric | Sulfuric | Citric | DL-Malic | Oxalic |
| 3. Less Hazardous Chemical Syntheses | ● | ● | ● | ● | ● | ● |
| 4. Designing Safer Chemicals | ● | ● | ● | ● | ● | ● |
| 5. Safer Solvents and Auxiliaries | ● | ● | ● | ● | ● | ● |
| 10. Design for Degradation | ● | ● | ● | ● | ● | ● |
| 12. Inherently Safer Chemistry for Accident Prevention | ● | ● | ● | ● | ● | ● |

In summary, the leaching processes studied in the references listed in Table 1 are based on the capacity of inorganic (nitric, sulfuric, hydrochloric) and organic (citric, oxalic, malic, succinic) acids to solubilize lanthanum and cobalt. While inorganic acids were applied almost exclusively to solubilize lanthanum, organic acids were largely used to solubilize cobalt. The use of an auxiliary reagent (e.g., hydrogen peroxide, ascorbic acid, glucose) has the aim of converting the metal in an oxidation state that in a further “recovery” stage of the process could form a less soluble compound. Specifically, several options are available to recover the metals from the leachates [12,13,20,27,29,31,35,42,43], including solvent extraction, ion exchange resins and precipitation. Focusing on precipitation, with the aim of considering a process compliant with the Green Chemistry principles mentioned in Table 2, the recovery of lanthanum and cobalt from the leachate may happen through various reagents. The use of sulfuric acid as a leaching agent was followed by the addition of NaOH to collect insoluble lanthanum sulfate at pH 2 [23] or by the addition of oxalic acid to collect insoluble cobalt oxalate [31]. The use of nitric acid as a leaching agent was followed by the addition of oxalic acid to collect insoluble lanthanum oxalate [12]. The use of hydrochloric acid as a leaching agent was followed by the addition of NaOH to collect insoluble Co(OH)₂ [35]. When organic leaching agents were adopted, direct recovery of cobalt oxalate was reported [42,43]. It is peculiar that the reuse of the liquor after the

recovery was explored only in one study [54], and lower leaching and further recovery efficiencies (compared to the virgin leaching agent) were reported. This is without any doubt an issue that needs further efforts in the future, in the perspective of optimizing a “green” process.

3.2. Experimental Conditions

The optimal experimental conditions reported by literature for lanthanum leaching involve the ranges of acid concentration, solid/liquid ratio, temperature, and contact time for the leaching process using inorganic acids (full boxes on the left of each plot) or organic acids (patterned boxes on the right) showed in Figure 3.

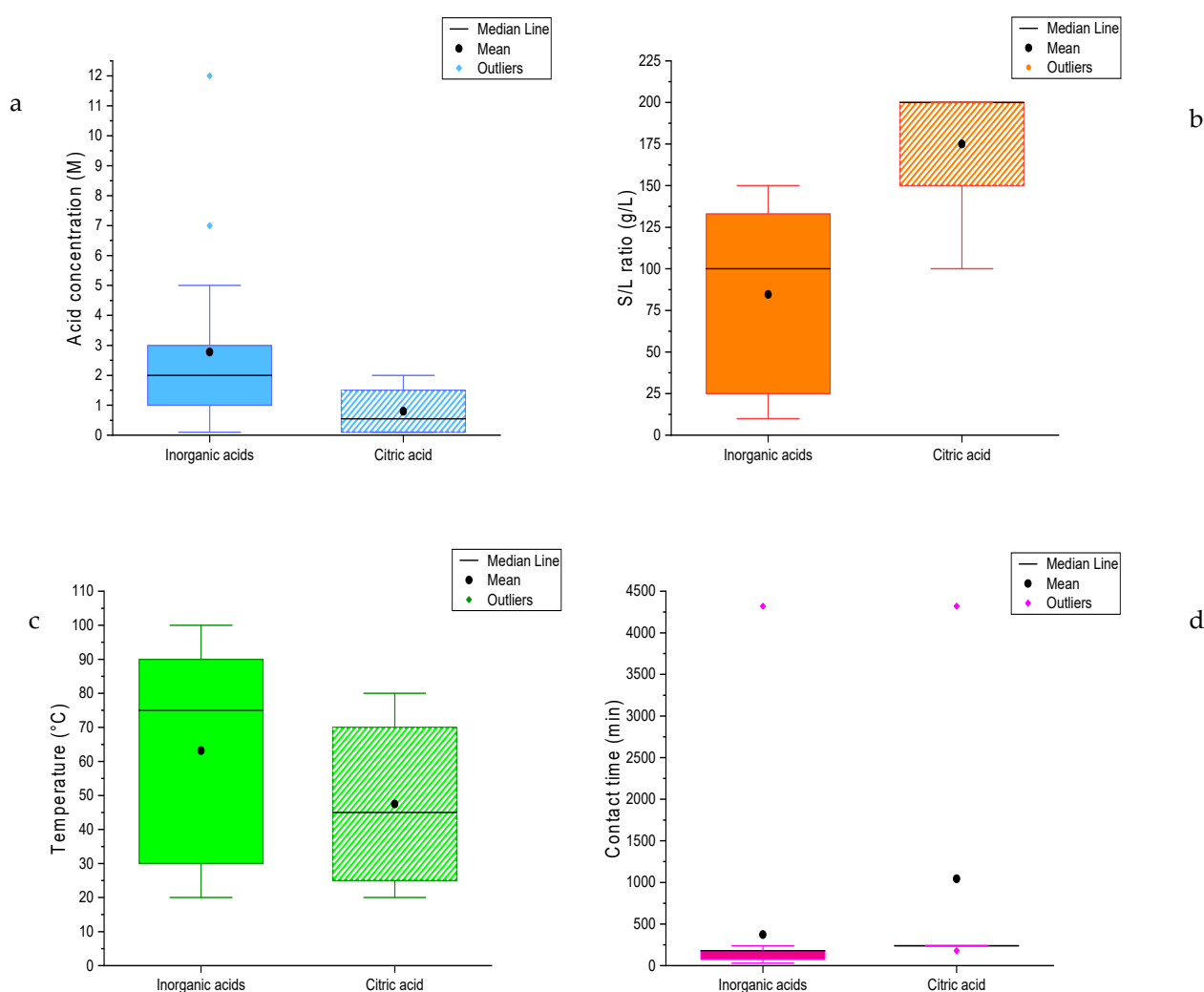


Figure 3. Box plots of the values of the experimental parameters for the recovery of lanthanum: (a) Acid concentration; (b) solid to liquid (S/L) ratio; (c) Temperature; (d) Contact time.

In the references selected for this review, the only organic acid used for lanthanum and REEs leaching was citric acid, which allowed to work with a more diluted chemical (median concentration 0.55 M) than the inorganic agents (median value 2 M) (Figure 3a). Processes using inorganic acids at different molarity have been developed, with concentrations ranging from 0.1 M to 12 M. The required solid to liquid ratio was higher in the processes that used citric acid (Figure 3b): the median value was 200 g/L, while the median mass leached by 1 L of inorganic acid was 100 g. Differently from the other considered parameters, the experimental temperature range of La leaching process did not change significantly with the nature of the acid employed (Figure 3c). The median temperature was higher (75 °C)

when the lixiviant is an inorganic acid, while for citric acid, the median value was 45 °C. Up to 72 h can be required to complete the leaching process (Figure 3d): the median value of the contact time was 3 h for inorganic acids and 4 h for citric acid. In conclusion, using diluted organic acids a higher amount of lanthanum can be leached at a lower temperature but extending the reaction time of the process.

The ranges of the experimental parameters employed for the cobalt leaching are reported in Figure 4. As seen for lanthanum, the needed concentration of organic acids for cobalt leaching was lower (ranging from 0.1 M to 2.5 M with 1.4 M as median value) than that of the inorganic ones (median concentration 2 M) (Figure 4a). The solid to liquid ratio was higher in the processes that used inorganic acids (Figure 4b): in this case, 1 L of lixiviant can treat the median mass of 50 g of waste material. On the contrary, the median solid to liquid ratio for organic acids was 20 g/L and the maximum experimental value found in the references was 50 g/L (4 times lower than the median solid to liquid ratio required to leach lanthanum using organic acids). The temperature range adopted in processes that used organic acids was narrow (Figure 4c), with higher values adopted when organic solvents (median experimental temperature 87.5 °C) were used instead of inorganic ones (75 °C). Lastly, while the median time needed to complete the leaching with inorganic acids was 75 min, the process with organic agents had a median duration equal to 85 min (but it can last up to 6 h) (Figure 4d).

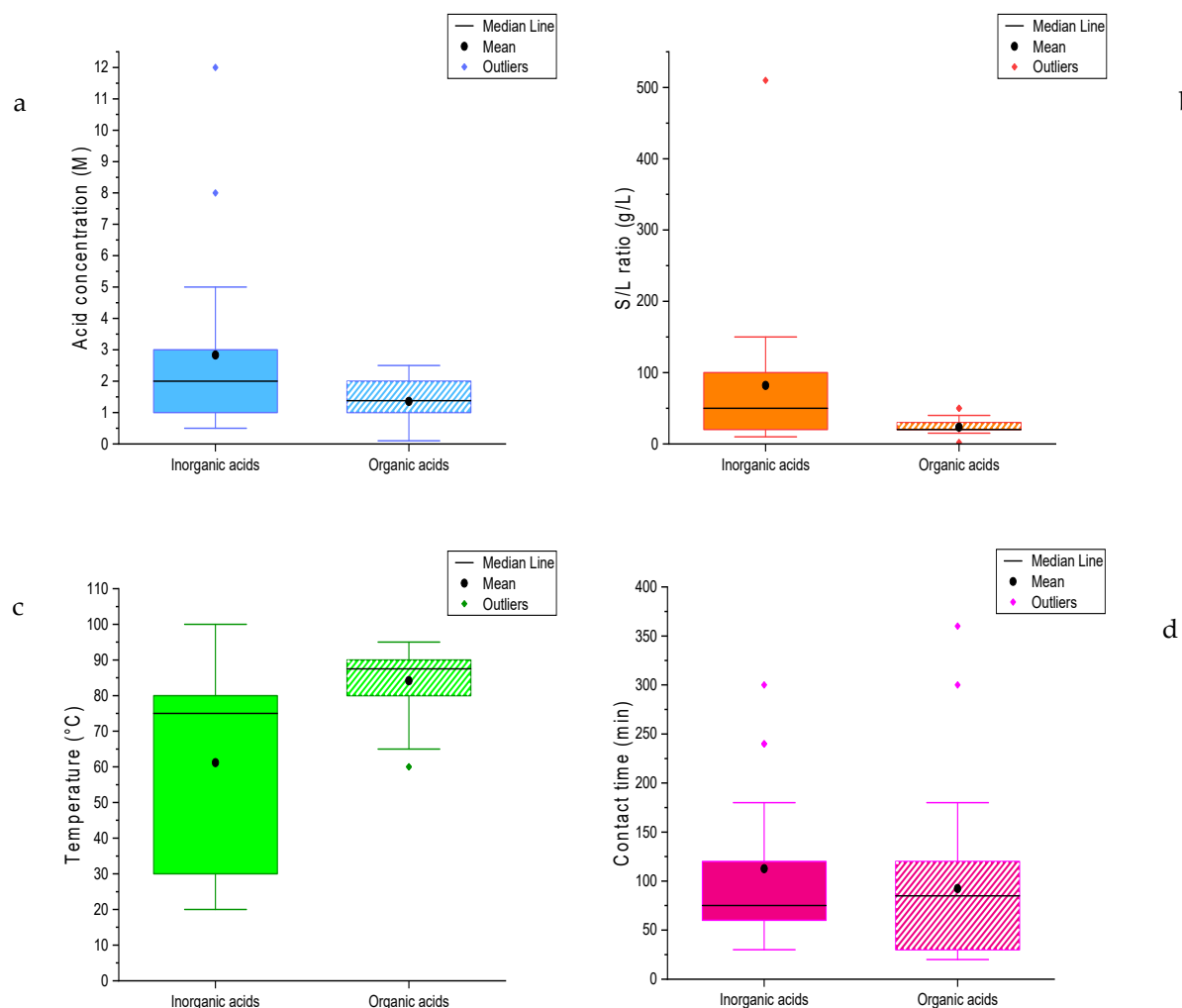


Figure 4. Box plots of the values of the experimental parameters for the recovery of cobalt: (a) Acid concentration; (b) S/L ratio; (c) Temperature; (d) Contact time.

As shown in Figures 3 and 4, broad ranges of values of the experimental conditions were proposed by the literature; therefore, the mean value of a parameter can be poorly representative of the real experimental conditions applied. For example, considering lanthanum leaching, five processes from a total of nine using inorganic acids proposed a contact time equal to 3 h (median value), while the mean value was 11.5 h (with a standard deviation even greater than 24 h). Therefore, to define the best conditions for lanthanum and cobalt leaching, Table 3 reports the median values of the experimental parameters found in the literature (irrespective of the nature of the acid employed). To leach lanthanum and cobalt in a single process, the following operative conditions (defined according to the ranges of median values in Table 3) can be adopted: acid concentration 1.5–2 M, solid to liquid ratio equal to 20–100 g/L, temperature equal to 70–80 °C and contact time 80–180 min.

Table 3. Experimental parameters proposed for the leaching processes of lanthanum and cobalt.

| Element of Interest | Median Value | | | |
|---------------------|--------------------|-----------|-------------|--------------|
| | Acid Concentration | S/L Ratio | Temperature | Contact Time |
| Lanthanum | 2 M | 100 g/L | 70 °C | 180 min |
| Cobalt | 1.5 M | 20 g/L | 80 °C | 80 min |

Alternative procedures described in the literature consisted of two leaching steps, exploiting the different solubility of lanthanum and cobalt in the acid lixiviant in the function of the process temperature. Innocenzi and Vegliò [28] proposed a two-phase leaching process based on sulfuric acid: the first phase at 80 °C to dissolve most elements except REEs, and the second phase at room temperature to maximize the REEs' solubility.

4. Conclusions

This review analyzed the scientific literature describing the leaching of lanthanum and cobalt from various waste materials, with the aim of exploring the up-to-date perspectives for the recovery of these critical raw materials from waste SOCs. The specific process investigated was the first phase of hydrometallurgical recovery—i.e., leaching. The analyzed processes were declared “green” if compliant with at least three of the five involved Green Chemistry principles (No. 3, 4, 5, 10, and 12). Most references (85%) focused on cobalt, fewer on REEs (and lanthanum). The involved leaching agents were largely (>80%) inorganic acids (nitric, sulfuric, hydrochloric), particularly for lanthanum, while also organic acids (citric, oxalic, malic, succinic) were considered, mostly for cobalt. According to the proposed definition, the leaching processes based on inorganic acids could not be considered “green”; on the contrary, all processes adopting organic acids fulfilled at least three of the considered five Green Chemistry principles.

Both for lanthanum and cobalt, the reported experimental conditions involved more diluted solvents if organic acids were employed (median value 0.55 M for lanthanum and 1.4 M for cobalt) instead of inorganic acids (median value 2 M in both cases). Organic acids required a higher solid to liquid ratio, compared to inorganic leaching agents, to solubilize lanthanum (200 g/L vs. 100 g/L), while the opposite happened for cobalt (20 g/L vs. 50 g/L). The process temperature did not change significantly with the nature of the leaching solvent (45–75 °C for lanthanum, and 75–88 °C for cobalt). The contact time was higher for lanthanum (median value 3–4 h) than for cobalt (median value 75–85 min). Considering the overall results of the literature survey performed, the experimental study of the leaching of lanthanum and cobalt in a single process could be based, irrespective of the nature of the adopted solvent, on an acid concentration equal to 1.5–2 M, a 20–100 g/L solid to liquid ratio, a temperature of 70–80 °C and contact time equal to 80–180 min. Surprisingly, the reuse of the acidic liquor after the recovery of the metals as insoluble compounds was explored only in one literature study. This is without any doubt an issue

that needs further efforts in the future, in the perspective of optimizing a “green” process. In conclusion, considering the urgent need for recycling processes specific for waste SOC, this review can provide some useful hints to define the experimental conditions to study the leaching of lanthanum and cobalt from waste cathodes of SOC.

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List of Abbreviations

CRM: critical raw material; EC: European Commission; EoL: end-of-life; EU: European Union; FC: fuel cell; GHG: greenhouse gas; HIMS: hazardous materials identification system; M: mol/L; REE: rare-earth element; S/L: solid to liquid ratio; SOC: solid oxide cell; SOFC: solid oxide fuel cell; USD: United States Dollar.

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