Integrating life cycle assessment and life cycle costing of fluorescent spent lamps recycling by hydrometallurgical processes aimed at the rare earths recovery

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ABSTRACT

This study compared the sustainability of two recycling treatments of fluorescent powders aimed at recovering rare earths. The analysis has been performed to evaluate the environmental impacts and economic aspects by using Life Cycle Assessment (LCA) and Life Cycle Cost (LCC). The first process includes a thermal pretreatment at 950 °C of powders, followed by sulfuric acid leaching, precipitation with oxalic acid and recovery of rare earths as oxides, and wastewater treatment. The second one differs only for the preliminary treatment; a mechanical activation has been proposed as an alternative to thermal pretreatment. The LCA proved the advantage of secondary production of rare earth oxides (REOs), compared to the current supply from ores. Furthermore, an environmental advantage of process A was estimated for combining the highest recovery and the lowest hazardous level of waste to dispose of, thanks to the preliminary removal of mercury. The potential benefit of REO recoveries was mainly highlighted in the categories of climate change and resource use, energy carriers and the leaching phase was identified as the main burden in most of the analyzed environmental categories. The final oxide from Process A contains more terbium than the product obtained from Process B. Labor is the main item of operating costs, and electric energy represents around 99% and 73% for Process A and Process B, respectively. The sensitivity analysis shows that varying the plant's capacity, the net profit increases. The main factor that influences the economic feasibility is the prices of rare earths.

1. Introduction

The amount of waste electrical and electronic equipment (WEEE) generated every year in the world is increasing rapidly. It is now one of the fastest-growing waste streams. Regarding the European Union, the current rules aim to reduce the waste and recovery of the contained materials. An efficient waste collection and management system can improve sustainable production and consumption, increase resource efficiency and contribute to the circular economy [1]. WEEE contains a complex mixture of materials, some of which are hazardous which can cause major environmental and health problems if the discarded devices are not managed properly. In addition, modern electronics contain rare and expensive resources, which can be recycled and re-used if the waste is effectively managed. WEEE are a mine of base materials (as copper, zinc,…), precious (gold, silver, platinum,.), and critical metals as rare earths. Among the WEEE with a relevant amount of rare earths are the fluorescent lamps. In the European Union, the total lighting devices (including fluorescent lamps) put on the market is increased from around 300,000 tons to 470,000 tons in 2011 and 2017, respectively. The total collected amount was increased from 17,666 tons in 2011–64,

413 tons in 2017. The study of 2015 shows that 32,773 tons of lighting devices have been treated; in 2017, 61,527 tons were recycled and prepared for reuse. The total amount of recycled devices has tripled since 2014 [2–4]. With a view to a more sustainable future and a circular economy, it is necessary to develop recycling processes for WEEE directed toward the recovery of base metals and critical materials as rare earths. In this perspective, the present manuscript describes two recycling processes for spent fluorescent lamps and analyzed their technical, economic, and environmental feasibility.

As already mentioned, fluorescent lamps have a relevant concentration of rare earths and are an important secondary resource. These elements are used for numerous advanced technological applications and classified as critical materials from European Union; in addition, the economic value of REEs strongly depends on the international market, considering also that China produces about 90% of the worldwide REEs from primary sources [5]. REEs are presents in the fluorescent lamps as phosphors, red phosphors $Y_2O_3:Eu^{3+}$ (YOX), green phosphors $LaPO_4$: Ce^{3+}, Tb^{3+} (LAP), $(Gd,Mg)B_5O_{12}:Ce^{3+}$, Tb_3 (CBT), (Ce,Tb) $MgAl11O19$ (CAT) and the blue phosphors $BaMgAl_{10}O_{17}:Eu_2$ (BAM) [6–8].

Other electronic devices using the properties of the rare earhs phosphors are the cathode ray tubes (CRTs), whose recycling is almost ended [9–11]. The amount of rare earths in the spent fluorescent lamps can reach 27.9%, but only 10% is recovered [12].

The first phase of the recycling process is a physical pretreatment to separate the phosphors from the other materials of the lamps (glass, aluminum, and other metals). After that, REEs can be recovered by using a pyrometallurgical or hydrometallurgical approach.

The low percentage of REE recovery depends on the high acid resistance of some type of phosphors. The red phosphors with Y and Eu are easily dissolved by diluted acid with respect to the other ones; instead, the other phosphors rich in terbium, gadolinium, lanthanum, and cerium are less easily leached and need specific pretreatments able to destroy or weaken the crystalline structure.

Yttrium is the most relevant rare earths in the fluorescent lamps, just an example the concentration of fluorescent materials obtained after industrial dismantling and sieving up to 38 μm is (% wt): Y= 11.21%, Ce= 0.49%, Eu= 0.44%, La= 0.38%, Tb= 0.27% and Gd= 0.25% [13,14]. Their accurate characterization is often difficult, but it is possible to apply mathematical models to determine the mineralogical composition of a mixture of solid phases by combining inductively coupled plasma spectroscopy (ICP) and electronic microprobe analysis (EMA) [15]. In the past, the recycling processes have been mainly developed for yttrium and europium [5,11,16–18], but, in recent years, the attention was also focused on the other rare earths, mainly terbium having the highest economic value. The main developed recycling processes for spent fluorescent lamps are based on hydrometallurgical and pyrometallurgical processes. The details of the scientific works aimed at the recovery of yttrium is reported in several reviews[5,19]. Instead, a list of the recently developed processes has been reported below. Terbium and other rare earths contained in the green phosphors need mechanical or thermal treatments. Mechanical process or mechanical activation (MA) can induce a modification in the properties of the solids and weaken the crystalline structure of the phosphors and thereby facilitate the following dissolution, and recovery phases [18,20–24] studied the mechanical activation applied to pure LAP. The studied effects were milling time, ball size, speed and ball to power ratio. The treated material was leached by using hydrochloric acid (4 N) at room temperature, obtaining the following dissolution yields: 99% for La, 87.3% for Ce, and 86.3% for Tb. Another series of experiments have been performed, which included leaching with methane sulfonic acid after MA of pure LAP. The solvo-mechanical approach increases the efficiency of the dissolution with respect to a simple MA coupled with sulfuric acid leaching. Tan et al. [25] reported their study for the recovery of rare earths from fluorescent powders. The process included: MA by ball milling and leaching with hydrochloric acid. The leaching yields were 89.4%,

93.1%, and 94.6% for terbium, europium and yttrium, respectively. MA was also applied to waste trichromatic phosphors by using a ball mill to study the effect of the speed on the following leaching stage. The results showed that MA improved the recovery rates of REE, almost doubling the extraction yields in comparison with un-milled phosphors. The maximum leaching efficiencies were 96.3%, 91.1%, and 77.6% for Y, Eu, and Ce, respectively.

Nevertheless, Tb was not monitored across the process [26]. Tan et al. [21] studied the effect of mechanical activation on waste phosphors dissolution. The results showed that the leaching yields for terbium increased from 2.5% (in the absence of MA) to a value greater than 73% (in the presence of MA). The experimental conditions were 600 rpm of the rotation speed of the ball mill and 1 M of HCl. The same research group investigated the effect of mechanical activation on the dissolution of the rare earth (Tb, La, Ce, Y and Eu). The results confirmed a significant enhancement of the leaching step [22].

Hasegawa [27] investigated the extraction of Ce, Eu, La, Tb, and Y from waste phosphors by applying combined MA-chelator treatments (dry and wet MA). Ethylenediaminetetraacetic acid (EDTA), ethylenediaminedisuccinic acid, methylglycinediacetic acid, and 3-hydroxy-2,20-iminodisuccinic acid were tested. The wet mechanical activation with EDTA gave the maximum extraction yields, but the duration of 6 h was rather long.

He et al. [23] tested Wet MA with NaOH, followed by leaching with sulphuric acid. Under optimal conditions, the maximum cerium and terbium extraction yield was 85.0% and 89.8%, respectively. Tanvar and Dhawan [18] studied the milling by a ball mill of fluorescent powders from discharged fluorescent lamps. The milling time (20–40 min) increased the leaching efficiency of the rare earths by using 3 M of inorganic acid (nitric, hydrochloric, and sulfuric acid). The dissolution enhanced from 35% (in the absence of milling) up to 85% (in the presence of milling). The alternative to the mechanical pretreatment is the thermal one. This phase includes an alkaline fusion, where the phosphors are roasted at high temperatures up to 950 °C with alkaline reagents (as sodium hydroxide[28], potassium hydroxide [29], barium hydroxide [14,30], and sodium carbonate [31]. A series of roasting of fluorescent powders from spent lamps with potassium hydroxide experiments have been performed at 900 °C for 1 h in a 1:1 wt ratio. After that, the treated materials were leached by using 5 M of HCl, 15% wt/vol pulp density, temperature 90 °C for 2 h. In these conditions, 80–90% of terbium dissolution was obtained. Rare earths were recovered as oxides after precipitation with oxalic acid and calcination at 600 °C. The solid had the following concentrations: concentrate composition expressed as oxides, was: Y 86.43%, Ce 4.11%, La 3.18%, Eu 3.08%, Tb 2.20% [30]. Yu et al. [28] tested the sodium hydroxide, and the sub-molten salt technique decomposed the blue and green phosphors structures at 280 °C with 70% of NaOH for 4 h. Y and Eu were mostly previously removed by chlorination roasting followed by the water leaching process. The rare earths in the residue were leached by using HCl after that were recovered at pH 7.5 by adding $NH_3 \cdot H_2O$ solution, and the impurities present in the precipitation can be removed by precipitation with oxalic acid. The final RE oxide was composed of 94.12% of Eu_2O_3, CeO_2, and Tb_4O_7. Thermal treatment at 950 °C for 1 h with $Ba(OH)_2$ was investigated by Ippolito et al. [14]. After that, rare earths were dissolved by using sulfuric acid, obtaining the following maximum yields: 99.8% of Y, 88.0% of Eu, 79.5% of Tb, 51.9% of Gd, 55.9% of Ce, and 43.0% of La. These elements were precipitated and recovered as oxides with a grade (98.62%). Therefore, a solvent extraction process with D2EHPA in kerosene has been suggested to separate the rare earths [32]. Yurramendi et al. [31] investigated the efficiency of the thermal treatment at different temperatures (200–900 °C) of phosphors/Na_2CO_3 mixture at different weight ratios for 1–3 h. The treated materials were leached by H_2SO_4 and HCl; thus, the REEs were extracted by D2EHPA in xylene. REEs were recovered as oxalates and finally calcined at 700 °C. The overall recovery efficiencies were 82%, 75%, and 82% for Ce, La, and Tb, respectively. In another scientific work, Liu et al. studied the alkaline

fusion of blue and green phosphors at 600 °C for 2 h. Y, Eu, Ce, and Tb-rich solutions were respectively obtained by the two-steps acidolysis. The leaching yields for T, Eu, Ce, and Tb were 96%, 99%, 81%, and 92%, respectively.

In this manuscript, a comparison between two recycling treatments for fluorescent powders of spent lamps has been performed aimed at rare earths recovery. The first process, Process A, consists of a thermal pre-treatment at 950 °C of initial materials 950 °C by using barium hydroxide, followed by sulfuric acid dissolution, and precipitation with oxalic acid to obtain rare earth oxides [14]. The second process, Process B, consists of a mechanical activation (MA), followed by sulfuric acid leaching, precipitation with oxalic acid, and calcination to obtain REEs oxides [33]. Furthermore, for both processes, lime wastewater treatment has been proposed to reduce the amount of residual spent leach liquors in agreement with the zero liquid discharge (ZLD) approach. The recovered water can be used for industrial purposes reducing the freshwater supply from industries. The two processes are simulated by using SuperPro Designer®. This work aims to assess the proposed recycling treatment to prove techno-economic and environmental sustainability. With this aim, the life cycle assessment (LCA) and the life cycle costing (LCC) analysis are carried out.

In our previous work [34], a study on the sustainability of the recycling processes for spent lamps, FCC spent catalysts, and permanent magnetic was described. Unlike the previous one, the present manuscript focuses only on recycling spent fluorescent powders comparing two hydrometallurgical processes. LCA and LCC methods were presented as tools to implement the principle of sustainable development in the circular economy, according to the current economic model promoted by the European Union that requires an use more sustainably of the resources.

In this perspectives, the integration of LCA and LCC analyses to waste and e-waste recycling has been crucial in order to the effective sustainability of the developed processes for a possible implementation on industrial scale.

Based on the authors' knowledge, no other scientific works analyzed the environmental and economic aspects of hydrometallurgical processes to recover REEs from this type of electronic waste. The result provides useful information for a possible investment relative to fluorescent lamps' recycling processes to meet the European objectives in this field of sustainability and circular economy.

2. Materials and methods

2.1. Chemicals and solutions

Experiments were carried out with wastewater obtained from fluorescent lamps recycling as described in our previous research. Leaching and precipitation of rare earths were performed by using sulfuric acid (Carlo Erba, >96%) and oxalic acid (Fluka, >97%), respectively [14]. The residual solution was analyzed to define the main chemical characteristics. The exact concentration of sulfuric acid was determined by potentiometric titrations. Whereas the exact concentration of oxalic acid was determined by titration with $KMnO_4$ (Sigma-Aldrich, 99%) considering a color change and related to the following reaction:

$$5\ H_2C_2O_4 + 2KMnO_4 + 3\ H_2SO4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 10CO_2 + 2\ H_2O \quad (1)$$
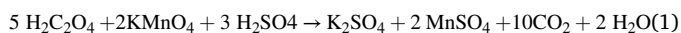
Calcium hydroxide solid (Sigma-Aldrich, >95%) has been used for precipitation of impurities.

Total suspended solids (TSS) were measured by Standard Method 2540 for solid determination in the water and wastewater treatment industry [35].

The precipitated solids were analyzed by X-ray fluorescence (XRF, Spectro Xepos) to define the main elements. A quantitative analysis was also carried out by Agilent Technologies 5100 ICP-OES atomic absorption after acid attack in order to evaluate the percentages of metals. The

acid attack was performed in a 25 mL closed flask as follows: around 0.5 g of initial material was dissolved with 1:3 of nitric acid (VWR Chemical, 65%) and hydrochloric acid (VWR Chemicals, 37%) at 90 °C.

2.2. Experimental procedure

Lime neutralization was carried out to study the efficiency of the precipitation treatment for the removal of impurities from residual wastewater from hydrometallurgical processes aimed at the recovery of rare earths from fluorescent powders. Lime neutralization of wastewater can be explained by the following reactions:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + H_2O \quad (2)$$

$$H_2C_2O_4 + Ca(OH)_2 \rightarrow CaC_2O_4 + 2H_2O \quad (3)$$
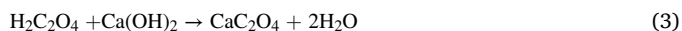
Experimental tests have been performed at room temperature and under stirring (200 rpm). The addition of lime has been performed step by step, increasing the pH value in the range (0.4–8.1). Several samples have been collected and characterized in terms of pH, and total suspended solids (TSS), total dissolved solids (TDS), sulfuric and oxalic acid concentration, and a selection of the main impurities.

2.3. Scope definition and background on process

The data obtained during the experimental tests showed that lime precipitation was efficient in removing impurities from residual leach liquors (LL). More in detail, the precipitation operation has been performed in two steps. The first one includes in solution pH up to 1.8, filtration, and separation of the solid and liquid. The solid is rich in calcium sulfate and can be recovered, while the solution can be further treated to increase the pH up to 8.1 and reduce the amount the impurities in the treated water. After this second step, the solid is separated from the liquid; the cake is a salts mixture and should be treated as solid waste; instead, the treated water can be reused as process water. This wastewater treatment has been proposed to treat the residual solutions coming from hydrometallurgical processes for the recycling of spent fluorescent lamps[14,33]. The aim is to reduce the amount of wastewater to disposal, maximize the water recovery and valorize, wherever possible, the salts contained in the residual solutions.

Hence based on research activity, two process schemes have been considered: the first, Process A, includes a thermal pre-treatment of the fluorescent powder conducted at 950 °C, followed by leaching with sulfuric acid, precipitation with oxalic acid, and finally calcination of the rare earth oxalates; the second one, Process B, provides for the replacement of the thermal pre-treatment with a mechanical activation, leaving unchanged the sequence of recovery operations (leaching, precipitation, and final calcination) [33]. Moreover, for both processes, wastewater treatment with lime has been considered. The life cycle assessment (LCA) and life cycle cost (LCC) of rare earth recovery from fluorescent powders was performed by hydrometallurgical processes according to previous experimental research and process analysis carried out by using specific software, Intelligen's SuperPro Designer® v9.5 (SPD). Mass and energy balances (M&E balances) and the equipment size are obtained as results of the simulation. These data have been used to perform a comparison between the two processes by life cycle assessment (LCA) and life cycle cost (LCC).

2.3.1. Functional unit and system boundaries

For the life cycle assessment and life cycle cost analysis, 100 kg per batch of fluorescent powders coming lamps has been chosen as a function unit. The characterization of the initial fluorescent lamps used for the research activity, as reported in the previous articles, is shown in Table S1 (Supplementary materials). Yttrium and europium oxides are red phosphors easily leached with an inorganic acid; instead, terbium, lanthanum, and cerium are present as green phosphors and structurally stronger than the red ones and need a preliminary treatment for

weakening the bonds of phosphates. The two alternative pre-treatments are the thermal process at 950 °C (Process A) and the mechanical activation (Process B) that are able to facilitate the subsequent recovery stages. A brief description of each operation of the proposed recycling processes is given below.

2.3.1.1. Process A: Thermal pre-treatment, leaching, precipitation and calcination. The system boundaries for the first recycling process have been shown in Fig. 1a.

The treatment included:

i) Thermal pre-treatment at 950 °C for 1 h in the presence of barium hydroxide (0.2%w/w) is described by reaction (4).

$$2REPO_4 + 3 Ba(OH)_2 \rightarrow RE_2O_3 + Ba_3(PO_4)_2 + 3H_2O \qquad (4)$$
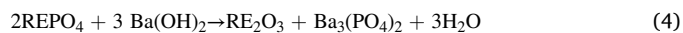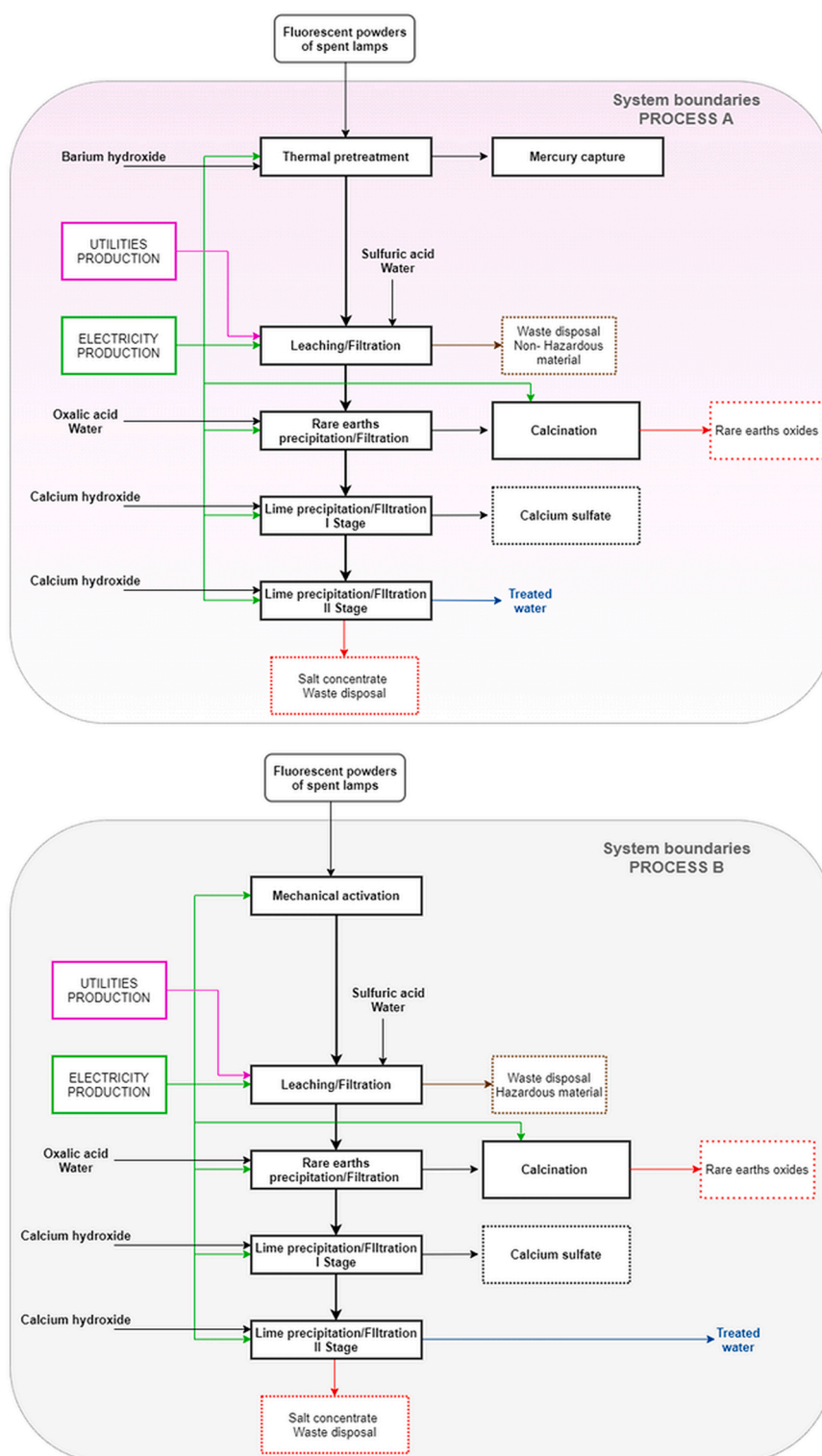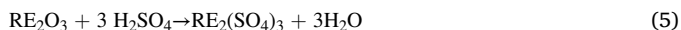
where RE are La, Ce and Tb.

Fig. 1. System boundaries for the proposed recycling processes for fluorescent lamps, (a) Process A; (b) Process B.

Two streams from the furnace were obtained: emission containing mercury and the calcined powders with residual barium hydroxide. The gas flow required cooling up to around 30 °C, and after disposal, the treated powder was sent to the chemical reactor for dissolution. The energy consumption for this operation has been estimated to be 82.17 kW; an amount of 305 kg/batch of chilled water is necessary to cool the gas flow coming from thermal treatment.

ii) Leaching with sulfuric acid 1 M, temperature 80 °C, 5% w/v of pulp density for 1 h (reaction 5).

$$RE_2O_3 + 3\ H_2SO_4 \rightarrow RE_2(SO_4)_3 + 3H_2O \qquad (5)$$

Where RE are Rare Earths (Y, Eu, La, Ce, Gd and Tb).

In these conditions the rare earths dissolutions were: 88.3% for yttrium, 99.6% for europium, 69% for terbium, 54.1% for gadolinium, 50.3% for cerium and 47.7% for lanthanum. After dissolution, the suspension was cooled up to 25 °C to decrease the solubility of calcium and barium sulfates that precipitated. The suspension was filtered to separate the unleached material and sulfates from liquid, the solid was washed, and the washing water mixed with leaching solution was sent to the precipitation step. The total energy consumption for mixing and filter press has been estimated at 4.62 kW. As regards the utilities, around 120 kg per batch of steam at 152 °C is necessary to maintain a leaching temperature of 80 °C, and 23,775 kg per batch of chilled water is used for cooling the suspension after the reaction.

iii) Precipitation with oxalic acid (12 g/L), temperature 25 °C, for 1 h (reaction 6).

$$2RE(SO_4)_3 + 3\ H_2C_2O_4 \rightarrow RE_2(C_2O_4)_3 + 6\ H_2SO_4 \qquad (6)$$
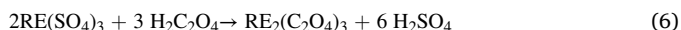
Where RE are Rare Earths (Y, Eu, La, Ce, Gd and Tb).

After the reaction, the products were washed to remove impurities and calcined to 600 °C for 1 h. The precipitation yields for rare earths were around 97%. The final products had the following grade (as oxides): 83.61%Y; 4.15% Eu, 1.13% Gd, 5.18% La, 2.26%Tb, 3.40% Ce [14]. The total grade was 99.73%, and silica (inert material) was the major impurity 0.26%, with traces of sulfates. Total energy consumption for mixing of precipitation reactor and filter press has been estimated to be 5.93 kW; instead, for calcination it has been supposed to use an electric furnace that needs 20 kW of energy.

iv) The last operation of the recycling process is wastewater treatment. As suggested by the experimental results, the residual leach liquor has been treated by chemical precipitation, adding calcium hydroxide to increase the pH and reduce the amount of pollutants. Experimental data have been implemented on the software for process analysis and to define the mass balance and energy of the process. Two precipitation steps have been considered; the first one produces a solid residue mainly consisting of calcium sulfate with rare earth hydroxides, and the second one produces a solid with residual calcium sulfate, calcium hydroxide, and other metal hydroxides. The first precipitate had the following grade 69.23% calcium sulfate, 29.82% of water, 0.04% calcium hydroxide, 0.06% oxalic acid, 0.36% of yttrium hydroxide, and 0.49% of traces of other metal hydroxides. This dry solid is almost completely calcium sulfates and could be sold or valorized. In the present manuscript, this first solid is considered a secondary product but zero economic value to perform a conservative analysis. The solid obtained from the second treatment step has the following composition: 56.59% of calcium sulfate, 13.06% calcium oxalates, 0.16% calcium hydroxide, 29.03% of water, and other metals hydroxides. Total energy consumption for mixing of precipitation reactors and filter presses has been estimated to be 11.96 kW.

2.3.1.2. Process B: Mechanical activation, leaching, precipitation and calcination.
The system boundaries for the second process have been shown in Fig. 1b.

i) The recycling treatment included: mechanical activation of the fluorescent material to weaken the crystalline structure and facilitate the dissolution of rare earths. The energy consumption for this operation has been estimated to be 27 kW [33].

ii) Leaching with 1 M sulfuric acid, 25 °C, 5% of pulp density for 1 h (reaction 4). In these conditions, the leaching yields were: 73% for yttrium, 99% for europium and gadolinium, 35% for terbium, 47% for cerium, and 49% for lanthanum[33]. The dissolution operation needs a slight cooling to maintain the temperature at 25 °C. After leaching, the suspension was filtered to separate the solid and liquid, the cake was washed, and washing water and acid solution were conveyed to the precipitation step. Total energy consumption has been estimated at 4.56 kW 0.180 kg per batch of chilled water is necessary for leaching operation.

iii) The precipitation operation is carried out under the conditions described for Process A. The final oxides has the following concentration (as oxides): 81.06% Y; 4.85% Eu, 2.41% Gd, 6.28% La, 1.34% Tb, 3.74% Ce. The total grade was 99.68% and silica (inert material) was the major impurity 0.32%, with traces of sulfates. The total energy consumption for mixing of precipitation reactor and filter press has been estimated to be 5.86 kW; instead, for calcination, it has been supposed to use an electrical furnace that needs 20 kW of energy.

iv) As for Process A, also in this case, the last operation is the wastewater treatment as already described.

Table S2 summarizes the mass balances of the Process A and B.

The mass balance showed that from 100 kg/batch of fluorescent powder, it is possible to obtain 18.83 kg and 16 kg of REEs oxide from Process A and Process B, respectively. The grade of the final oxides is 99.73% and 99.68% a Process A and Process B, respectively. The main difference is the % of Tb on the final product, in the first case is 2.26% (Process A) instead of in the second one is 1.34% (Process B), this depends on the different performance of the leaching operations and could influence the cost-effectiveness of the recycling processes. Regarding the waste, the amount of the unleached material is almost similar for the two processes (around 170 kg/batch), but the residual solid from Scenario B is more hazardous because it contains mercury (0.006%). In the first process, mercury is removed during the pre-treatment at 950 °C; therefore, it is supposed that the disposal cost is higher for Process B. Anyway, in Process A, mercury in the emissions should be disposed of, and another treatment cost should be added. The different operations require energy and utility consumption, shown in Table S3.

2.3.2. Methodology

The mass and energy balances have been used to carry out LCA and LCC analysis to assess both the environmental and the economic impact of the considered options. The life cycle assessment was performed according to the LCA ISO standards 14040 and 14044:2006 [36,37]. The estimation of the environmental impacts, combined with the LCC, aims to identify the most sustainable scenario in implementing a sustainable circular economy. The steps of classification, characterization, normalization, and weighting were included within the LCA. The thinkstep Gabi software 9.5, combined with Gabi Professional Database (version 8.7) were used for the analysis. The method selected for the assessment was Environmental Footprint 3.0 (including impact categories, recommended models at the midpoint, indicators, units, and sources) [2, 38–40]. Some assumptions were performed for the analysis:

- The oxalic acid production process (not present in the reference database) was built using the information reported by Santoro et al.

[41] and Murad and Khalaf [42], in agreement with the process described by Amato et al. [34].

- The recovered REOs were considered as environmental credit for the avoided impact for their primary production.
- The hazardous level of leaching solid waste from Process A has been assumed lower than that from Process B, thanks to the previous removal of Hg.
- The impact of treated water from the lime precipitation step was assumed 0 for its possible recirculation within the further process batches.
- The recovered calcium sulfate has been considered with a 0 impact for its possible re-use. The value '0' ensured conservative conditions, compared to an environmental credit.

The last three assumptions have also been performed for LCC. The economic evaluation of the two recycling processes has been performed by using the LCC approach [43,44], considering the recurring cost (RC) and the non-recurring cost (NRC):

$$LCC = RC + NRC \tag{7}$$

RC are the labor costs (per year), more in detail: operational energy costs and maintenance (and repair) cost, purchase cost for the reagents, and costs for waste disposal (Operating Expense, OPEX). Instead, NRC are the capital investment, including the equipment cost (PEC), piping system, and engineering, amortized in X years. Capital Expenditure (CAPEX) has been estimated from PEC, based on which total costs (direct and indirect) have been calculated (FCI-fixed Capital Investment), contributing to the determination of the total capital investment (TCI). PEC was obtained from vendors or by using literature data [45]. 2002 was the reference year for the equipment cost, and the values have been discounted at 2020 by using the CEPCI – Chemical Engineering Plant Cost Index [46].

Table S4 shows the main processing units required for each process. Table 1 reports the capital costs for the proposed processes, including purchase, installation, electrical service, instruments, buildings site development, ancillary buildings, design and engineering, contactors' fee, and contingencies [45].

Table 2 shows the operative costs (€ per batch), instead Table S5 and S6 (supplementary materials) report the unit price of reagents and utilities, respectively. For maintenance it has been considered 3% of FCI.

Labour costs have been calculated considering one operator per batch (50 €/h for 8 h/batch). Moreover, it has been added the operating supervision is estimated to be 5% of the labour cost. Financial indicators as net present value (NPV), Payback time (PBT), and Return on Investment (ROI) are estimated by using Excel software.

3. Results and discussion

3.1. Wastewater treatment

The principal aim of these experiments was to reduce the amount of impurities as residual rare earths, calcium, and other metals in wastewater to reuse the treated water as process water and avoid disposal costs due to the treatment in a specific plant. The results, reported in Fig. S1 and Table 3, showed that this operation can precipitate and remove the impurities with high efficiency.

Fig. S1 reports the sulfuric acid and oxalic acid concentration as a function of pH: complete removal of acids is obtained at pH 8.1.

Table 1
Capital costs for recycling Process A and B (€).

	Process A	Process B
Fixed Capital Investment Cost (FCI)	1,144,678.95	1,264,562.63
Working capital	171,701.84	189,684.39
Total Capital Investment Cost (TCI)	1,316,380.79	1,454,247.03

Table 2
Variable operating parameters (€/batch, 1 batch = 100 kg of fluorescent powder).

Consumable and raw materials (€/batch)		
	Process A	Process B
Sulfuric acid (pure)	41.60	39.20
Oxalic acid (pure)	48.00	48.00
Water	2.96	2.80
Barium Hydroxide (pure)	14.00	–
Calcium hydroxide (solid)	8.00	16.00
Total	114.56	106.00
Utilities (€//batch)		
	Process A	Process B
Electricity	19.5	11.25
Chilled water (5–10 °C)	6.50	0.05
Steam (152 °C)	0.34	–
Total	26.34	11.30
Other (€/batch)		
	Process A	Process B
Waste Management (Transport and Landfill)	61.07	55.2
Maintenance and repairs	114.47	126.46
Personnel cost	200	200
Total	516.44	489.93

According to the results of the experiments, at pH 1.4–1.8 the recovered solid is mainly calcium sulfates. (Fig. S2, S3). After filtration step leach liquors with pH= 1.8 can be treated with lime up to pH= 8 in order to have parameters under limits.

The solids were analyzed after drying at 105 °C for 24 h by XRF. The data of XRF and ICP (Table 3) are investigated, and according to consumption of lime, stoichiometric reactions between the main substances and calcium hydroxide, and precipitation yields the estimated composition has been obtained (Fig. S3).

The first dried solid obtained at pH 1.8 has a high concentration of calcium sulfate (around 98,60%) and 1.4% of traces of other substances as calcium oxalate (0.52%), yttrium hydroxide (0.43%), calcium hydroxide (0.28%), and 0.17% of other (as aluminum hydroxide). The second solid has a significantly lower calcium sulfate concentration (12.76%). The main compound is calcium oxalate (51.67%), followed by calcium hydroxide (23.31%), 0.13% yttrium oxalate, and 12.13% others (as aluminum and iron-manganese hydroxides).

These results suggested that the lime precipitation process was an effective technique for treating residual wastewater after leaching and precipitation of rare earths. The first solid is mainly calcium sulfate which could have a market value. Such solid is a by-product, but no economic value has been associated; calcium sulfate is indeed produced in large amounts worldwide, and it could be challenging to find a market. Instead, the second precipitate has been considered waste to dispose of, with an associated cost.

These preliminary data from experimental tests have been used to propose a wastewater treatment after leaching and rare earth precipitation and implemented for the process analysis, as described in the following sections.

3.2. LCA results

Considering the high efficiency of the proposed processes, the combination of environmental and economic evaluations is essential to determine the stakeholders' choices involved in the fluorescent powder exploitation. From a technical point of view, Process A showed a more complex pre-treatment with a higher energy demand than Process B. Nevertheless, the highest consumptions were combined with the highest recovery of REOs (mainly yttrium and terbium oxides). In this context, the LCA has proven to be an excellent tool to drive the most sustainable choice between lower consumptions/lower recovery efficiency and higher consumptions/greater recovery in environmental terms. Overall, the results of classification and characterization phases (Fig. S4) showed

Table 3
Composition of residual leaching residue before and after adding lime.

	Ca (OH)$_2$, [g/L]	pH	SST [g/L]	SDT, [g/L]	H$_2$SO$_4$, [g/L]	H$_2$C$_2$O$_4$, [g/L]	Al, [mg/L]	Y, [mg/L]	Fe, [mg/L]	P, [mg/L]
Wastewater	0	0.4	0	134.4	40.5	7.7	984	227	42.4	1163
1	65.0	1.4	108.9	21.5	2.2	6.4	916	12.7	42.2	857
2	66.6	1.8	138.8	21.3	1.4	5.3	882	8.9	41.2	783
3	67.6	2.5	142.4	20.2	0.5	3.6	851	2.2	36.5	724
4	69.6	3.4	143.4	12.1	0.2	0.5				
5	76.6	8.1	163.9	0.02	0	0.3	0.64	0.004	0.008	0.058

comparable impacts between the two proposed options since the highest environmental load of Process A had been compensated by the greatest credit of recovered REOs, in most of the considered categories. More in detail, the environmental advantage can be explained by the contribution of europium, yttrium, and terbium oxides, respectively around 50%, 30%, and 18% of the whole environmental credit. The main advantage of yttrium oxide is connected to the highest recovered amount, whereas the benefit of both europium and terbium oxides is explained by the greatest environmental load of their primary production, avoided thanks to the lamp recycling. Regarding environmental impacts, leaching represents the main criticality, and the highest negative effect in Process A is mainly due to the greatest utility consumptions. Another relevant impact is that of sulphuric acid use (with an environmental burden higher than 10% in most of the considered categories). Different results can be observed for the human health effects since hazardous waste disposal represents the main issue in these categories. The preliminary separation of mercury in process A has been translated into reducing the hazardous level of final solid waste to dispose of. Furthermore, the results of classification and characterization supply important directions for the further process scale-up, identifying the main criticalities to focus on during the optimization phase (e.g., the decrease of utility consumption, the introduction of renewable energy resources for the electricity production or/and the development of a high efficiencies recirculation system of flows, able to increase the whole environmental sustainability).

The results were confirmed by the normalization and weighting steps which identified Process A as the best option. The possibility of the highest recovery of yttrium, europium, and terbium oxides decreased the environmental footprint by about 20%. More in detail, this index was expressed in-person equivalent (p.e.), i.e., the number of average citizens which generate a comparable impact in one year [47,48]. The further focus on the most affected impact categories (pie chart in Figure5, the impact categories with a contribution lower than 2% have been included in "others") confirmed that the most relevant issues of the recovery processes are: the human effects, mainly due to the hazardous residue disposal, and the ionizing radiation, mainly due to the energy consumption for utilities supply/production. As already mentioned in the classification and characterization phases, the preliminary mercury removal allowed the lowest contribution of human health effects in process A.

On the other hand, the lowest utility consumptions of leaching in Process B reduces the effect on the ionizing radiation category. The connection between utility production and ionizing radiation category is the energy consumption with the possible production of radionucleotides from nuclear energy production and the mineral oil and gas extraction, used as energy carriers[34,49]. Furthermore, the study of the affected categories during the primary production of REOs (Fig. 2, the pie-chart on the lower right) highlighted the potential benefit on both climate change and resource use, energy carriers resulting from their secondary production from fluorescent powders. Identifying the environmental credit in these categories represents essential information to confirm the process potential in a European scenario. Indeed, both the resource conservation and the decrease of climate change emissions represent a current priority, as confirmed by the G20 Rome leaders'
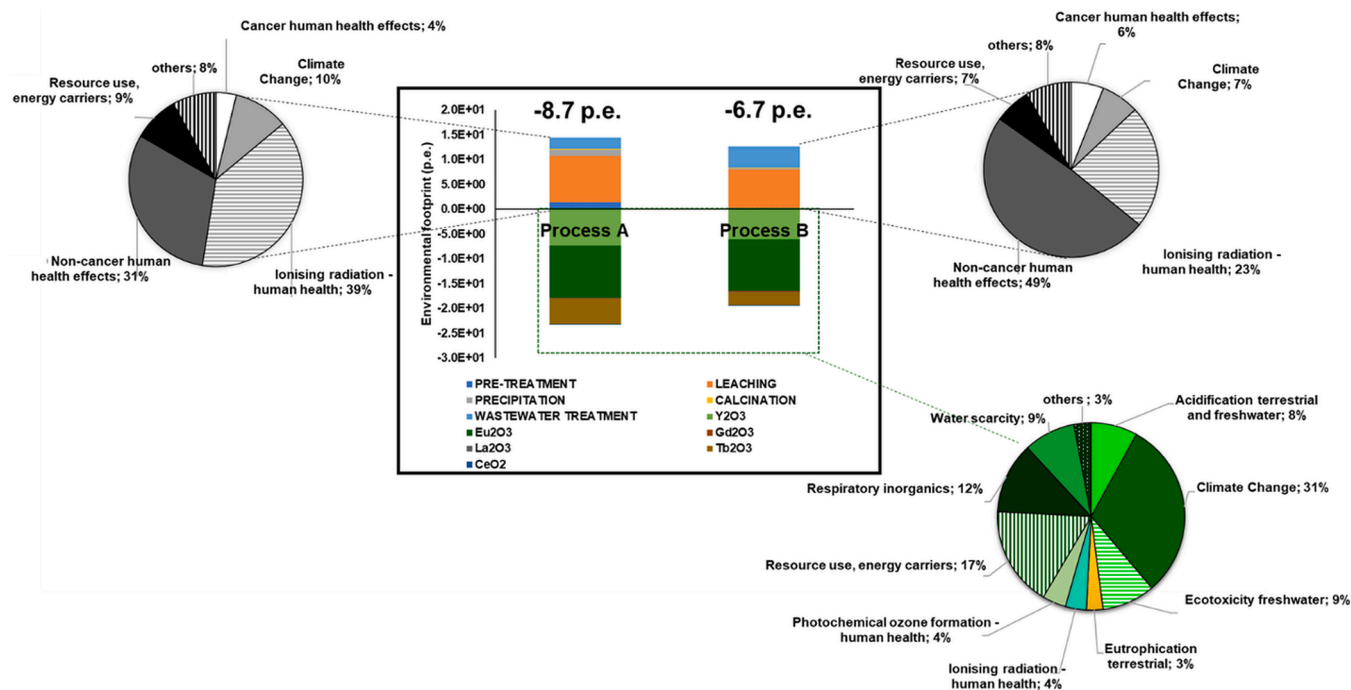
Fig. 2. Results of normalization and weighting phases of LCA. The pie charts show the most affected impact categories ("others" includes the impact categories with a contribution lower than 2%).Functional unit: 100 kg of fluorescent powders.

declaration and the COP26 goals.

3.3. LCC results

The life cycle costs for Process A and B are reported in this section. Fig. S5 (Supplementary materials) shows the total cost (€/batch) that included the Capital Cost (comprised of insurance and taxes of 2% of FCI), reagents, labour, maintenance and repairs, utilities (chilled water, steam, electricity) and waste management.

Other items have been added for the final estimation of the annual net treatment cost (NPC) (see Table S7, Supplementary materials). The depreciation had a significant incidence on total cost, followed by operating labor and supervision. The higher cost for utilities in Process A was due to higher electrical energy consumption, mainly during the thermal pre-treatment. Fig. S6 shows the details of the OPEX (€/batch). The data confirms that the personnel item is the most important of the other operating costs.

Electricity is 99% and 73% of the total utility cost (Fig. S7) for mechanical and thermal treatments, respectively. For Process B, the mechanical pre-treatment represents about 40% of the total; instead, for Process A, the thermal pre-treatment has the 65% of the electricity consumption. Identifying the most relevant items is essential to define the most economically sustainable process and, if possible, improve the recovery treatments to reduce the operative costs and the economic impact.

3.4. Economic feasibility

3.4.1. Base case specific analysis

Preliminary economic feasibility of Process A and B has been reported. The net profit is calculated considering the total cost described above and the revenue obtained from the sale of rare earth oxides. More in detail, the economic price of the final product has been calculated considering the current value of the REO reduced by 70% to take into account that they are not pure and their percentage on the mixture. In this case, the total economic value of REO is around 225 €/batch and 112 €/batch for Process A and B, respectively (Fig. S8, Supplementary materials). Terbium oxide is the most important rare earth among the considered ones. The final oxide of Process A contains more terbium respect than the recovered solid by Process B. Among the revenues, the credit for the disposal of fluorescent lamps has been considered. More in detail, considering that phosphors are 3% of the total amount of lamps, to produce 100 kg of initial materials, around 12,820 lamps are necessary (about 0.260 kg per lamp). The recycling cost for lamps has been assumed of 0.63 €/kg [50]. In this item, the avoided disposal of the fluorescent lamps in landfills is considered (0.4 €/kg). Instead, the

possible revenue from the selling of aluminium and glass is not considered. Fig. 3 shows the comparison between the cost and the revenues.

The analysis shows that the processes are economically feasible; it is important to note that 95% of the total revenues are due to the lamps treatments' credit. In the absence of this issue, the processes are not economically sustainable with the current prices of REO also by altering the number of batch/day up to a maximum of three per day.

The financial indicators (NPV, PBP, and ROI) for Process A are better than those of Process B; in fact, the NPV over 10 years is nearly 345 k€, to have a positive net present value for the Process B is positive after the eleventh year. PBPs are 4.7 and 6.5 years for Process B and A, respectively; instead, the data of ROI are near to 21% and 15% for Process A and B, respectively.

A sensitivity analysis has been performed in order to check the feasibility of the process.

The market of rare earths influences the economic balance of the recycling treatments. Given the importance of these materials for several technological fields, their economic value on the market varies greatly; just consider that the price in 2011 was 20, 100 times higher than now, for yttrium and europium oxide. A similar situation was for La and Ce oxide, which have seen a 50 fold price reduction in recent years.

In this manuscript, a sensitivity analysis has been performed considering the price of the rare earth oxides in 2011. In the analysis, it is also considered to increase the scale of the plant. The details of the sensitivity analysis have been reported below.

3.4.2. Sensitivity analysis

The sensitivity analysis has been carried out by varying the price of the REO and the plant capacity. In the first study, the 2011 cost of REO was considered (100 kg/batch of fluorescent powder): this was the maximum value in the last years; after that, it has been assumed a maximum variability of rare earth oxide price of + 50%, with respect to the current value, and reduced again by 30% to consider that the final oxide is a mixture of rare earths). Fig. 4 reports the first sensitivity analysis, the net profit (€/y) as a function of the REO market prices.

The credit from the lamp recycling treatment item is still the largest in the profit calculation; in correspondence with the REO price of 2011, the revenues from the selling of the final oxides is 35% of the total ones.

Moreover the profitability is influenced by the size of the plant, for that it has been varied the amount of initial fluorescent powder in the range 100–1000 kg/batch. This range of values has been chosen taking into account the current estimated lamps waste generated in Italy [52]. Even though the plant's capacity has increased, the recycling processes are not yet economically feasible with the current sale prices. The revenues reach nearly 5000 k€/y when increasing the capacity of
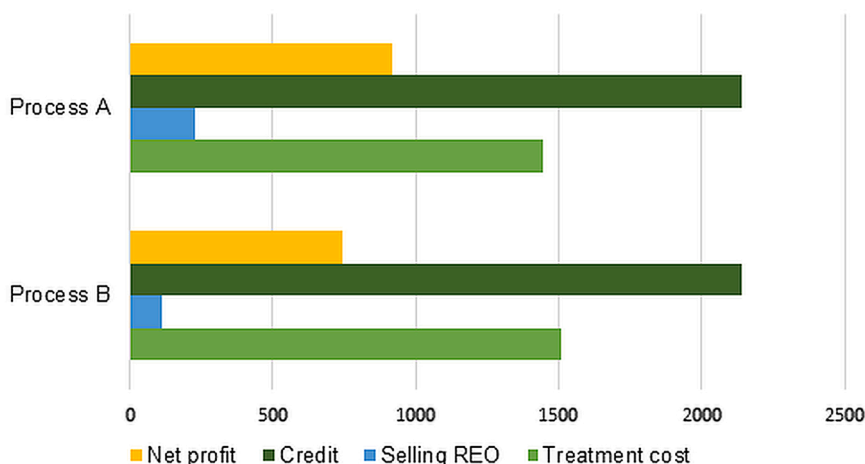

Fig. 3. Treatment cost and revenues (€/batch) due to the REO selling and lamps recycling treatment credit.

Fig. 4. Net profit (k€/y) as a function of the rare earths price variations.

fluorescent powders per batch.

3.5. The estimation of climate change cost

The present paper assessed the environmental and economic process costs. Nevertheless, another aspect that should not be neglected is the economic cost of the environmental impacts, mainly the greenhouse gas emissions, which represent a hot topic as confirmed by the European Green Deal and the even more recent G20. Following the German Environment Agency (UBA) recommendation, Table S8 reports the climate costs estimated for the two analyzed processes, compared to the primary supply of REOs, using a cost rate of 180 €/tons CO_2 equivalent [51].

Despite the possible variation of the emission costs, the estimation showed a relevant advantage of secondary production of REOs, with a benefit of Process A of 12%, compared to option B. The estimation drew attention to the important aspect of the long-term costs for the environmental impact management, highlighting the possibility to convert an avoided impact into an economic saving. This kind of approach should become a practice on the sustainability assessment of processes.

4. Conclusions

The combination of technical, environmental, and economic aspects has proved to be an effective method to assess the sustainability of recycling processes. Two case studies for the treatment of fluorescent powders from lamps have been investigated to recover rare earths. Both approaches include wastewater treatment with lime to produce treated water that can be reused. The proposed process schemes allowed the recovery of rare earth oxides and water by a zero liquid discharge treatment. Process A results in the best yields of rare earth recovery (mainly for terbium) thanks to thermal pretreatment. Hence, the final oxides have a higher economic value than those obtained with the second process. LCA and LCC have been performed considering the mass and energy balances obtained from process analysis (100 kg of fluorescent powders per batch). The LCA highlighted the relevance of REOs recovery, showing an advantage of around 20% of the Process A. The analysis showed that the benefit of this option is mainly connected to the highest environmental credit of secondary europium, yttrium, and terbium oxides (able to balance the most significant environmental impact of the treatment) and a preliminary mercury separation. The environmental advantage of the fluorescent powder exploitation was also confirmed by the climate cost estimation, which showed an advantage of about 80%, compared to the primary production of the same amount of resulting REOs. The total treatment cost (€/batch of fluorescent powders) was 695 and 633 for Process A and B, respectively. The net profit considering the selling prices for the final oxides and the credits for lamps recycling is 276 k€/y and 224 k€/y for Process A and B, respectively. The sensitivity analysis shows that the rare earths market greatly influences the profitability of the recycling treatments. This issue represents a limit for a possible industrial application as economic

sustainability is closely linked to market fluctuations. Besides that, the plant size affects the profitability and considering the total amount of fluorescent lamps waste generated in Italy yearly and the current prices of rare earths, the processes are economically feasible if a credit for lamps recycling is provided.

CRediT authorship contribution statement

Nicolò Maria Ippolito: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Alessia Amato:** Methodology, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Valentina Innocenzi:** Conceptualization, Methodology, Data curation, Writing – original draft, Writing – review & editing. **Francesco Ferella:** Conceptualization, Methodology, Data curation, Writing – original draft, Writing – review & editing. **Francesca Beolchini:** Supervision. **Veglio Francesco Vegliò:** Supervision.

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.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.107064.

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