Selective Extraction of Red Phosphor (Y$_2$O$_3$:Eu^{3+}) Constituents from Waste Fluorescent Lamps Phosphor Using Acid Leaching

Parul Johar*ᵃ, Vishal Jangir*ᵇ, Yogita Choudharyᶜ, & Sudhanshu Mallickᶜ

ᵃDepartment of Energy and Environment, TERI School of Advanced Studies, New Delhi, India
ᵇCentre for Converging Technologies, University of Rajasthan, Jaipur, India
ᶜDepartment of Metallurgical Engineering and Materials Science, IIT Bombay, Mumbai, India

Students: joharparul@gmail.com*, yogitta.choudhary@gmail.com, jvishalcct013.nano@gmail.com*
Mentor: mallick@iitb.ac.in

ABSTRACT

Modern fluorescent lamp phosphor powder contains tricolor phosphor. This tricolor phosphor consists of three different types of rare earth phosphors: red (YOX), green (CMAT/LAP) and blue (BAM); mixed in varying proportions. The exact separation of these three rare earth phosphors is essential in order to precisely recover the contained rare earth elements from waste lamps phosphor. In this present work, we reported an efficient methodology for the separation of these three tricolor phosphors and the selective extraction of predominantly presented red phosphor (YOX) constituents using acid leaching. The waste phosphor powder was leached with different acids: both organic and inorganic type. The 3 M H$_2$SO$_4$ leaching was found to be most suitable for the selective extraction of red phosphor constituents, *i.e.* Y and Eu. The recovered phosphor powder was analyzed with SEM/EDS and XRD analysis. The obtained XRD pattern was refined using Rietveld refinement method for the quantification of phases present. Recovered red phosphor powder contained three main crystalline phases Y$_2$O$_3$, Eu$_2$O$_3$ and Y$_2$OS$_2$.

KEYWORDS

Waste Lamp Phosphor; Tricolor Phosphor; Rare Earth Elements; Acid Leaching

INTRODUCTION

The rare earth elements (REEs), which include 15 lanthanides, Y and Sc are essential for the development of various advanced technologies including efficient lighting, wind turbines, and hybrid electric vehicles. Moreover, their global demand is forecasted to continue with increasing rate of 3.7%-8.6% per year.[1] The primary sources of REEs extraction are mining of various natural deposits, *e.g.* bastnaesite, xenotime, and monazite *etc.* and ion-adsorption ores, contain varying amount of different REEs. Although their mining production and separation are considered difficult because these elements share similar chemical properties and have associated environmental concerns with their extraction.[2] To overcome both sustainable supply and environmental issues, an alternative approach as their efficient recovery from waste products i.e. urban mining is considered. Urban mining is emerging as an efficient source for REEs extraction and continuously receiving great attention towards their recovery from the end of life (EoL) products containing permanent magnets, phosphors, and NiMH rechargeable batteries.

Among all other EoL products, waste fluorescent lamps (FLs) are considered as the major source for REEs recovery since hundreds of millions of units of FLs are produced and discarded every year globally. As reported in the previous studies it is suggested that FLs phosphor often contributes to 2-3% of the total mass of a FL[3,4] and contains about 23% of REEs.[5,6] Modern FLs phosphors are typically composed of white calcium halophosphate and rare earth triphosphors, whose composition varies across manufacturers. These rare earth triphosphors are the mixture of red, green and blue rare earth phosphor with the varying composition and contain Y, La, Eu, Gd, Ce, and Tb as the key REEs **(Table 1)**.[7-9]

Currently, various approaches are being employed for the recovery of REEs from lamp phosphors including hydrometallurgy[4, 10, 11] pyrometallurgy[12], supercritical liquid extraction[13], electrometallurgy[14], and mechanical activation method.[15] Among all these approaches, hydrometallurgy is most widely accepted for the selective recovery of REEs because of its large operational scale, low energy circulation and low investment cost with high extraction yield especially for Y and Eu[16, 17] Y and Eu have special attention during the recovery of various REEs from waste lamp phosphors due to the high intrinsic value of Y$_2$O$_3$:Eu^{3+} as red rare earth phosphor present in them.[17, 18]

Hydrometallurgy typically includes leaching process followed by precipitation and solvent extraction to dissolve, separate and recover pure REEs. Generally, different acids, *e.g.* HCl, H$_2$SO$_4$, HNO$_3$, and alkalis, *e.g.* NaOH and NH$_3$ are employed as leaching agents. The leaching efficiencies for Y and Eu along with Ca are much higher than others like Ce, Tb, and La, this is due to easy dissolution of calcium halophosphate and YOX in dilute acids.[19] Under the conditions of pressure leaching of the waste phosphor blend, the leaching efficiencies for Y and Eu were achieved about 96.4% and 92.8%, respectively.[4] According to the previous studies, not much work has been done on the separation of red, green and blue rare earth phosphors,

obtained from real waste fluorescent lamps. Otsuki[20] used two liquid flotation process using N, N-dimethyl formamide (DMF) and heptane to separate $Y_2O_3:Eu^{3+}$, $LaPO_4:Ce^{3+}$, Tb^{3+}, and $(Sr,Ca,Be,Mg)_5(PO_4)_3Cl:Eu^{2+}$ three different lamp phosphors. Mei[21] separated red ($Y_2O_3:Eu^{3+}$), blue ($BaMgAl_{10}O_{17}:Eu^{2+}$) and green ($CeMgAl_{10}O_{17}:Tb^{3+}$) rare earth phosphor from synthetic rare earth triphosphor mixture using liquid/liquid extraction, 2-thenoyltrifluoroacetone (TTA) and potassium sodium tartrate depressant (PST) used to extract blue and red phosphor, respectively while chloroform used to extract green phosphor. Schaeffer[22] used a Brønsted acidic ionic liquid, *i.e.* 1-methylimidazolium hydrogen sulfate ([Hmim][HSO_4]) at the place of H_2SO_4 for the recovery of $Y_2O_3:Eu^{3+}$ (YOX) from waste fluorescent lamp phosphor.

Type of phosphor	Potential compounds	The approximate amount in tricolor lamp phosphor
Red	$Y_2O_3:Eu^{3+}$ (YOX)	55%
Green	$(Ce,Tb)MgAl_{11}O_{19}$ (CMAT) $LaPO_4:Ce^{3+},Tb^{3+}$(LAP)	35%
Blue	$BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM)	10-15%

Table 1. The appropriate chemical composition of tricolor rare earth phosphors used in modern FLs.

With respect to the above-mentioned issues, here we present an efficient methodology for the separation of red phosphor (YOX) from waste FLs phosphor mixture and its treatment to recover Y and Eu. The method used in this work incorporates the use of different leaching agents including various organic and inorganic acids for recovering REEs from the red phosphor. Further processes like precipitation and calcination were applied to separate the red phosphor constituents and to recover them. The challenges associated with recovery which include purities and concentrations of recovered REEs were also examined.

MATERIALS AND METHODS
Materials
The waste phosphor sample, collected from end-of-life FLs after removal of mercury, was provided by a leading Indian e-waste recycling company (Eco Recycling Ltd., Mumbai). As the leaching reagents; sulfuric acid (98%), citric acid, and *aqua regia* (HCl: HNO₃, volume ratio 3:1) were employed. The 3 M H_2SO_4 was prepared by diluting the sulfuric acid (98%) with pure water. Sodium hydroxide and oxalic acid were used for the pH adjustment and precipitation of leaching residues to obtain REEs oxalates, respectively. All the chemicals used in this work were of analytical grade and used without any further purification.

REEs			Other elements		
Element	Mass (wt. %)	Element	Mass (wt. %)	Element	Mass (wt. %)
Y	18.1	**Ca**	11.0	**Al**	1.9
Eu	1.7	**P**	11.8	**Mn**	0.6
Ce	1.6	**O**	10.2	**Zn**	1.4
Tb	2.2	**Ba**	1.4	**Si**	0.3
La	1.6	**Mg**	0.4	**Cl**	0.5
Gd	2.9	**Sr**	3.8	**Pt**	28.5

Table 2. The Elemental content of waste lamps raw phosphor powder sample (EDS).

Phase name	Chemical formula	Fraction (wt. %)
BAM	$Ba_{0.9}Eu_{0.1}Mg_2Al_{16}O_{27}$	7.71
Fluorapatite	$Ca_5(PO_4)_3F_{0.94}Cl_{0.1}$	7.95
CMAT	$Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19}$	10.41
YOX	$(Y_{0.95}Eu_{0.05})_2O_3$	16.69
Hydroxylapatite	$Ca_{9.42}Sr_{0.18}H_{0.4}(PO_4)_6(OH)_{1.60}$	26.96
Coesite (Quartz)	SiO_2	30.29

Table 3. Weight fraction of each phase present in the raw waste phosphor sample; resultant from structure refinement of obtained XRD pattern using the Rietveld refinement method.

A report on the detailed characterization of this investigated waste phosphor sample has already been submitted elsewhere. Here, in the present paper, the results obtained we have also added the chemical composition results obtained from waste phosphor sample analysis. The preliminary elemental composition of waste phosphor sample was determined using EDS and ICP-AES analysis. The obtained EDS analysis results for various REEs and other elements are given in **Table 2.** XRD

analysis was done to confirm the presence of various phases; this was followed by the structure refinement of obtained XRD pattern using Rietveld refinement method for the quantitative analysis of the phases and elements presented **(Table 3)**.
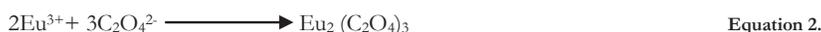
Experimental methodology
a. Acid Leaching
Preliminary leaching tests were performed using various acids including both inorganic and organic acids as leaching reagent; in order to find out the appropriate leaching reagent to obtain the high recovery yield for REEs. These leaching reagents were sulfuric acid (3 M and 18 M), *aqua regia* (HCl: HNO_3; volume ratio 3:1) and citric acid. Initially, 0.1 g of waste fluorescent lamp phosphor sample was dissolved into these different leaching reagents. The traditional *aqua regia* was employed since it is generally used to dissolve various metals. Two different molarities of sulfuric acid, 3 M and 18 M used to check its potential to dissolve all three rare earth phosphor present in waste phosphor sample. The citric acid was employed as an organic leaching agent, to recover REEs in an environmentally friendly manner. Some of the leaching parameters as the leaching temperature and solid to liquid (S/L) ratio (w/v) kept constant at 90 ℃ and 40%, respectively for each leaching experiment performed, moreover according to the available literature, the optimized leaching time for sulfuric acid[11] and *aqua regia* was kept constant at 4 h. The leaching time for citric acid leaching experiment was varied from 1 h to 2 h to reveal its potential for employing it as the suitable organic leaching agent.

b. Precipitation and calcination
The change in pH of the leached solution of the phosphor was observed using pH meter and adjusted to 2.4 using sodium hydroxide solution for the further ease of separation of the constituent elements by precipitation. The precipitation of obtained filtrate was done using the oxalic acid to convert the rare earth elements present into their respective oxalates. The precipitate i.e. rare earth oxalates obtained from the leachate was filtered and dried. The dried precipitate was kept in the muffle furnace in an alumina crucible at 750 ℃ for 6 h. This process was performed for the conversion of rare earth oxalate into their respective rare earth oxides. The possible chemical reactions that took place during the precipitation of the Y and Eu into their respective oxalates and the calcination of these oxalates in order to decompose them into their respective oxides are given below:

$$2Y^{3+} + 3C_2O_4^{2-} \longrightarrow Y_2(C_2O_4)_3 \hspace{3cm} \text{Equation 1.}$$

$$2Eu^{3+} + 3C_2O_4^{2-} \longrightarrow Eu_2(C_2O_4)_3 \hspace{3cm} \text{Equation 2.}$$

$$2Y_2(C_2O_4)_3 + 3O_2 \longrightarrow 2Y_2O_3 + 12CO_2 \hspace{2cm} \text{Equation 3.}$$

$$2Eu_2(C_2O_4)_3 + 3O_2 \longrightarrow 2Eu_2O_3 + 12CO_2 \hspace{2cm} \text{Equation 4.}$$

The complete experimental methodology used for the separation of tricolor phosphor and recovery of red phosphor is shown schematically in **Figure 1**.
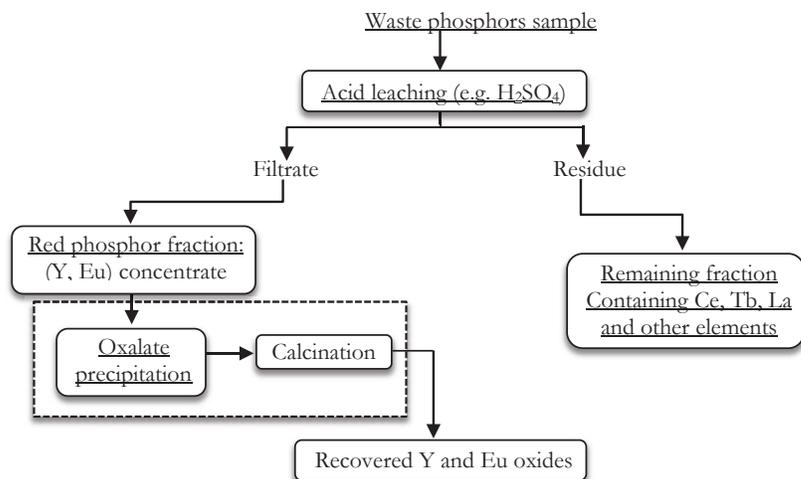

Figure 1. The experimental methodology used for the selective separation of red phosphor (YOX) and recovery of its constituents.

c. Analytical techniques
The chemical composition of the raw waste phosphor powder sample was analyzed using ICP-AES analysis. This technique was also used to determine the dissolution yield of the various elements in the leached liquor. The surface characteristics, morphology and elemental qualitative information of the resultant calcined powder of rare earth oxides were revealed using

SEM (JEOL JSM-7600F) along with EDS. The main crystalline phases present in the recovered rare earth oxide powder were analyzed using XRD (EMPYREAN, PANalytical) analysis; operated at 45 kV tube voltage and 40 mA tube current with the Cu-Kα (λ= 1.54 Å) radiation and the scanning was performed between 0° to 90° using continuous scanning mode. Further, the structure refinement of obtained XRD data was done by using the Rietveld refinement method with FullProf software for quantitative phase analysis.

RESULTS AND DISCUSSION

Effect of different leaching agents on leaching rates of elements

Table 4 shows the extracted fractions of various elements as the function of different acids leaching of waste phosphor sample measured using ICP-AES (SECTRO ACROS). As seen from the results, it is possible to conclude that the solubility of the predominant calcium halophosphate and red phosphor constituents was much higher in the 3 M H_2SO_4 leaching since they both readily dissolve in the diluted acids.[19]

	Y	Eu	Ce	Tb	Gd	La	Ca	P	Sr	Al	Mg	Ba	Si	Sb	Mn
SA (3 M)	18.55	1.75	0.07	<0.01	<0.01	0.06	19.55	9.21	0.09	1.34	0.03	0.02	0.31	0.36	0.28
SA (18 M)	16.41	0.84	0.7	<0.01	<0.01	1.03	17.55	8.84	0.12	0.64	0.02	0.01	0.19	0.33	0.25
CA (1h)	4.73	0.06	0.05	0.03	<0.01	<0.01	9.13	n.d.*	0.03	0.67	0.08	0.19	n.d.	n.d.	n.d.
CA (2h)	3.37	0.16	<0.01	<0.01	<0.01	<0.01	3.95	n.d.	0.01	0.21	0.1	0.12	n.d.	n.d.	n.d.
AqR	2.86	0.95	0.02	n.d.	<0.01	<0.01	17.61	8.86	0.09	2.67	0.06	0.08	0.57	n.d.	n.d.

Table 4. Element extraction obtained using different acids as leaching agents (wt. %) (SA= Sulfuric acid; CA= Citric acid; AqR= *Aqua Regia*; *not determined).

The major advantage of using H_2SO_4 leaching is that it provides high rates of extraction for Y and Eu due to the low solubility of formed $CaSO_4$ (gypsum), which is the major impurity to the leach liquor.[11] The results suggest that the other REEs (*e.g.,* Ce, Tb, La) contributed from the green and blue type phosphor were extracted in the much higher extent when waste powder was leached using concentrated (18 M) H_2SO_4 since they have highly stable chemical structure of spinel type and requires alkali roasting before acid leaching to destroy their spinel chemical structure.[23]

Figure 2 reports the extracted fraction of four major elements including Y and Eu as a function of treatment with the different types of leaching agents. The highest contribution of Y and Eu to the leach liquor was found to be 18.55% and 1.75% respectively for the 3 M H_2SO_4 leaching. This trend was also observed with the calcium halophosphate constituents (*e,g.,* Ca, P) as the Ca was also extracted in higher extent about 19.55% when treated with 3 M H_2SO_4 as compared to the 18 M H_2SO_4 leaching. This is probably due to the formation of the low solubility of $CaSO_4$.

The leaching experiments performed using citric acid did not provide satisfactory results as both the REEs and other elements were extracted in very limited extent which shows that it is not suitable as the leaching agent for the recovery of red phosphor constituents since the extraction of Y was found to be only about 4.73% which is too low with respect to the other acid leaching experiments. The similar behavior was seen using the *aqua regia* as leaching agent (Y extraction was only 2.86%). The maximum number of elements (about 15) were extracted using H_2SO_4 (3 M as well as 18 M) leaching and other employed leaching agents were not able to extract more than 12 elements.
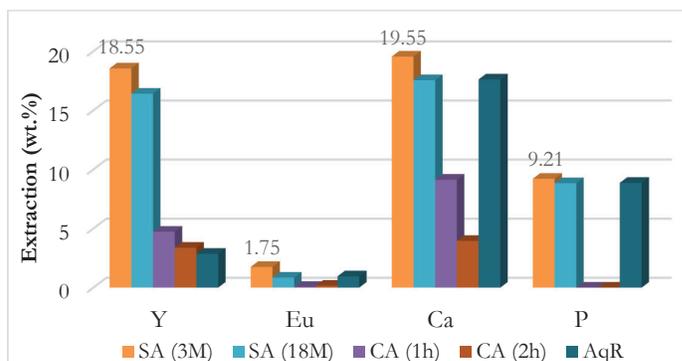

Figure 2. Extraction of major constituents of YOX and HALO phosphor obtained by various acid leaching of waste phosphor powder.

Selective extraction of red (Y_2O_3:Eu^{3+}) phosphor constituents

As the 3 M H_2SO_4 leaching was found satisfactory for the leaching of Y and Eu, the obtained filtrate was precipitated by the addition of oxalic acid. The obtained precipitate was filtered and dried overnight. Finally, this dried oxalate powder was calcined in order to produce the respective Y and Eu oxides.

a. SEM/EDS results

Figure 3(a) shows the characteristic micrograph of the obtained powder constituents as the densely packed flake-like morphology recovered using 3 M H_2SO_4 acid solution. All the elements were uniformly scattered as inferred from the EDS spectrum **(Figure 3(b))**. These obtained results clarify the existence of both Y and Eu as the major constituents in the recovered phosphor powder which are the major constituents of the red phosphor.
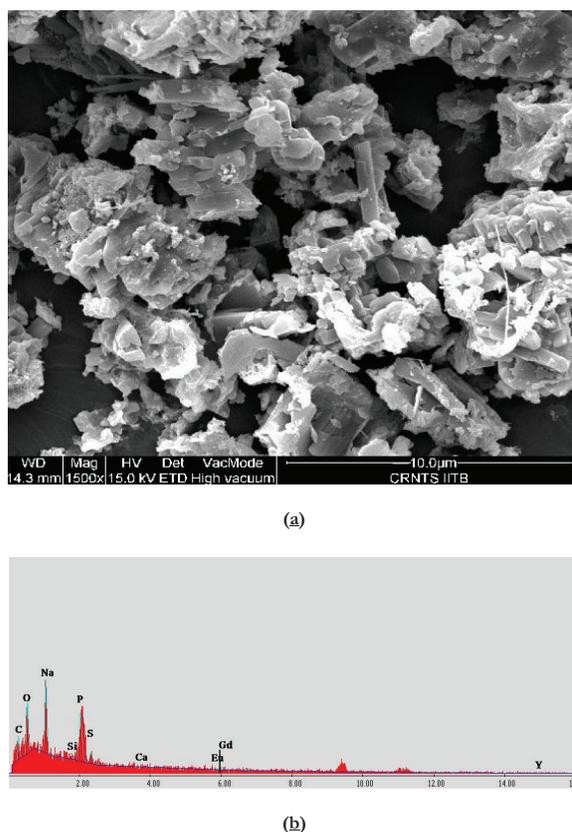

(a)

(b)

Figure 3. (a). SEM micrograph & (b). EDS spectrum of recovered red rare earth phosphor constituents.

As shown in **Table 5**, the yttrium and europium were found in the concentration of about 33.19% and 1.25% respectively. The appearance of Gadolinium in the obtained spectrum is significant to the presence of Gd_2O_3 phosphor in minor amount along with the YOX as the red rare earth phosphor[24] in the waste phosphor sample and earlier this was also observed from the obtained ICP-AES results of waste phosphor sample **(Table 4)**.

Element	Y	Eu	Gd	P	S	Si	Na	O	C
Mass (wt. %)	33.2	1.2	1.9	5.2	1.6	0.5	10.2	21.2	24.7

Table 5. EDS analysis of recovered red phosphor powder.

The Si and Na appeared as minor impurity elements possibly due to leached quartz particles and added NaOH for the pH adjustment respectively. The impurities from other REE phosphors (e.g. BAM and CMAT) were not detected in recovered phosphor powder, these results suggest the successful separation of the red phosphor from other waste phosphor constituents.

b. XRD and Rietveld refinement results

Figure 4 shows the X-ray diffraction pattern of recovered phosphor powder by using dilute (3 M) H_2SO_4 acid leaching along with the possible phases present. The major crystalline phases have been identified by their respective JCPDS cards Yttrium oxide (Y_2O_3; JCPDS 00-041-1105), Europium oxide (Eu_2O_3, JCPDS 00-034-0072) and Yttrium oxide sulphide (Y_2OS_2,

JCPDS 01-079-2251) along with the three minor impurity phases namely, quartz (SiO_2, JCPDS 00-012-0708), sodium oxalate ($Na_2C_2O_4$, JCPDS 00-049-1816) and calcium phosphate ($Ca_3(PO_4)_2$, JCPDS 00-009-0169). The identified sodium oxalate phase is possibly present due to the remaining oxalate precipitate even after the calcination process, this clarifies that the calcination temperature should be higher than 750 °C for the complete decomposition of the generated oxalate precipitates. The presence of quartz phase is mainly due to the leached quartz impurities from the waste phosphor sample.
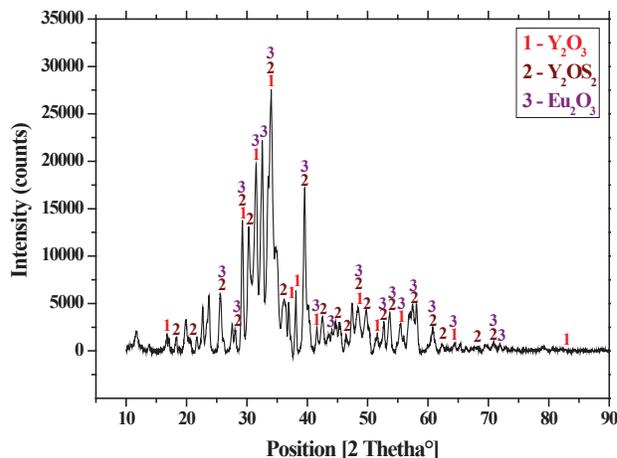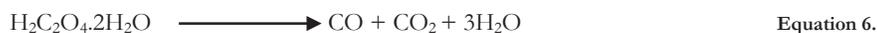

Figure 4. – X-ray diffraction pattern of the recovered red phosphor powder along with the three main crystalline phases present.

Figure 5 shows the refined X-ray diffraction patterns for the recovered phosphor powder as refined using the Rietveld refinement method. The diffraction pattern was refined, starting from the crystallographic parameters of Y_2O_3[25] and then further refined by the crystallographic parameters of other phases: Eu_2O_3[26], Y_2OS_2[27]. Finally, the minor impurities phases were refined in the sequence of SiO_2[28], $Na_2C_2O_4$[29] and $Ca_3(PO_4)_2$[30], respectively.

Y_2OS_2 was identified as the major phase (41.71%), this formation of yttrium oxide sulfide during the calcination process took place was likely due to a chemical reaction occurred between the yttrium sulfate which obtained from 3 M H_2SO_4 leaching (**Equation 5**) and the generated carbon monoxide due to the thermal decomposition of the remaining unreacted oxalic acid (**Equation 6**).[31,32] During the 3 M H_2SO_4 leaching, the red phosphor ($Y_2O_3:Eu^{3+}$) was converted into yttrium sulfate and europium sulfate and further this yttrium sulfate was precipitated into yttrium oxalate by the use of oxalic acid in order to recover yttrium oxide. The precipitation step requires a stoichiometric amount of oxalic acid and an optimum pH in order to precipitate yttrium sulfate into its respective oxalate.

It is assumed that due to an imbalance in the pH of the obtained leached solution, some fraction of present yttrium sulfate was not precipitated into yttrium oxalate which led yttrium sulfate and oxalic acid to remain unreacted into leached solution. This remained unreacted oxalic acid was thermally decomposed into carbon monoxide during the calcination at 750 ℃ (**Equation 6**).[31]

The possible chemical reactions that took place in the formation of yttrium oxide sulfide during the calcination process are given below:

$$(Y_{0.95}Eu_{0.05})_2O_3 + 3H_2SO_4 \longrightarrow Y_2(SO_4)_3 + Eu_2(SO_4)_3 + 3H_2O \qquad \text{Equation 5.}$$

$$H_2C_2O_4.2H_2O \longrightarrow CO + CO_2 + 3H_2O \qquad \text{Equation 6.}$$

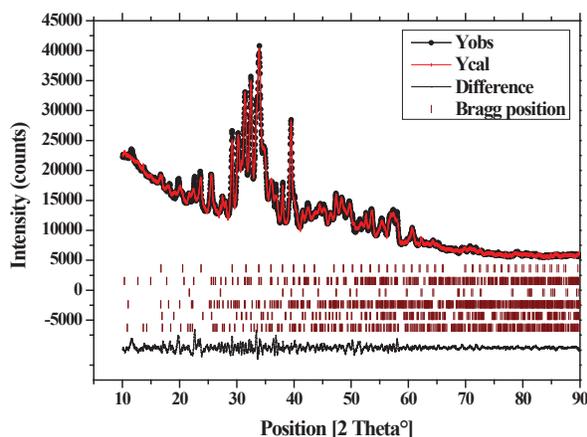$$Y_2(SO_4)_3 + 11CO \longrightarrow Y_2OS_2 + 11CO_2 + S \qquad \text{Equation 7.}$$

Figure 5. Observed (Yobs), Calculated (Ycal) and difference X-ray diffraction profiles for phosphor powders mixture. The vertical bars indicate the position of Bragg reflections for the various phase present. (*for Y_2O_3, Eu_2O_3, SiO_2, Y_2OS_2, $Na_2C_2O_4$ and $Ca_3(PO_4)_2$ from upper to lower, respectively).

The quantified amount of the various phases present in the recovered phosphor powder as resultant from the Rietveld refinement of the observed diffraction pattern is shown in **Table 6**. These results confirm that the major fraction of recovered phosphor powder obtained from the treatment of raw phosphor powder by using dilute (3 M) H_2SO_4 acid contains red phosphor constituents, *i.e.* Y and Eu. Two major compounds were found for Y - Y_2O_3 and Y_2OS_2 accounting for about approx. 60% of the total fraction. Another important phase present was Eu_2O_3 which accounted for about 24.68% as the second major rare earth oxide recovered. This high amount is possible due to the presence of Eu in both YOX and BAM rare earth phosphor. The remaining undecomposed fraction of sodium oxalate was found to be 13.40%. $Ca_3(PO_4)_2$ was found in very low amount due to the formation of calcium sulfate which has low solubility and it was filtered out with the remaining green and blue phosphor filtrate which shows that most of the calcium halophosphate had been filtered which as an advantage of using dilute (3 M) H_2SO_4 leaching over leaching by other acids. The minor impurities fraction of SiO_2 was also found. The recovery percent of yttrium and europium were calculated ca. 73% and ca. 71%, respectively.

Phase name	Fraction (wt. %)
Y_2OS_2	41.71
Y_2O_3	18.14
Eu_2O_3	24.68
$Na_2C_2O_4$	13.41
$Ca_3(PO_4)_2$	2.04

Table 6. Weight fraction of phases present in recovered red phosphor powder resultant from structure refinement using the Rietveld method (excluding the SiO_2 impurity phase, *i.e.* assuming 100 wt. % of remaining five red phosphor crystalline phases).

CONCLUSIONS

The waste phosphor powder mostly contains many valuable REEs in the mixture of their respective oxides as in the form of the tricolor phosphor. The work represented in this research was mainly focused on the recovery of red phosphor constituents and the separation of tricolor phosphors as the treatment of waste phosphor powder sample with the various type of inorganic and organic acids. After the detailed characterization of waste phosphor sample (submitted for publication elsewhere, the red phosphor was separated from the green and blue phosphor by the treatment of waste phosphor with 3 M H_2SO_4. The 3 M H_2SO_4 leaching was found suitable in order to recover the Y and Eu to a higher extent in comparison to the other leaching acids employed. The recovered phosphor powder mainly contained three crystalline phases - Y_2O_3, Eu_2O_3, and Y_2OS_2 as identified from the obtained diffraction pattern. The refinement of the diffraction pattern provided the quantified amount of phases identified, these three major phases accounted for about 60% of the total amount of recovered red phosphor powder.

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ABOUT STUDENT AUTHORS

Parul Johar graduated from The Energy and Resources Institute (TERI) School of Advanced Studies in June of 2017 with a major in Enviromental studies and resource management. She is currently pursuing her Ph.D. in chemistry at University of York, England. Yogita Choudhary graduated from the Indian Institute of Technology Bombay in June of 2018 with major in Metallurgical Engineering and Materials Science and specilization in Ceramics and Composites. She is currently working for Cairn, India. Vishal Jangir is currently pursuing his Masters of Technology with major in Nanotechnology at Center for Converging Technologies, University of Rajasthan. Vishal plans on pursuing Ph.D. This project was carried out by students authors while pursuing their undergraduate studies.

PRESS SUMMARY

The tricolor phosphor present in the waste fluorescent lamp phosphors consists of three different type of rare earth phosphors: red (YOX), green (CMAT/LAP) and blue (BAM) which are mixed in varying proportions. These three rare earth phosphors should be separated individually in order to precisely recover the contained rare earth elements into them. This current study reports an efficient methodology for the separation of these three tricolor phosphors and the selective extraction of predominantly presented red phosphor (YOX) constituents using acid leaching. The waste phosphor powder was leached with different acids: both organic and inorganic type. The recovered phosphor powder mainly contains the Y and Eu compounds which confirmed the successful extraction of red phosphor from waste fluorescent lamp phosphor.