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Green Chemistry

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ARTICLE TYPE

Photochemical recycling of europium from Eu/Y mixtures in red lamp phosphor waste streams

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Europium is one of the most critical rare-earth elements due to the combination of a high demand for the production of red lamp phosphors and the limited supply of this element.. Hence, the recycling of europium from end-of-life lamp phosphors has gained a lot of interest. Separation of europium from rare-earth mixtures can be done very efficiently by selective reduction of Eu(III) to Eu(II) and subsequent
10 removal of Eu(II) by $EuSO_4$ precipitation. Present study shows that full separation of europium from non-equimolar binary europium/yttrium mixtures, which reflect the rare earth composition of red lamp phosphors, can be achieved by photochemical reduction of Eu(III). Eu/Y molar ratios up to 1/20 were tested in the presence of an isopropanol radical scavenger, a less harmful and toxic compound than the commonly used formic acid scavenger. Moreover, in contrast to using the very acidic formic acid, higher
15 pH values could be reached with isopropanol, which is advantageous for the formation and the stability of the reduced Eu(II) species. Faster europium removal was obtained at higher pH values up to pH 4, halving the illumination time to reach 88 % of europium recovery. Efficiencies of over 95 % were reached, with purities of 98.5 % of the $EuSO_4$ precipitate. Europium recovery of industrial YOX powder was also achieved from a Eu/Y 1/30 ratio, with 50 % yield of $EuSO_4$ and a purity of 96 %.
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Introduction

Recently, the rare earths gained a lot of interest, since they are used in many high-tech applications and sustainable technology (permanent magnets, nickel metal hydride batteries, lamp
25 phosphors).[1,2] Europium, one of the most critical rare earths, has a high market value due to its use in the red lamp phosphor $Y_2O_3{:}Eu^{3+}$.[3] Because of the scarcity of europium on the global market, recycling of europium from lamp phosphor waste streams has become increasingly important.[4-13] Very recently, Dupont and
30 Binnemans reported on a novel process to selectively recover $Y_2O_3{:}Eu^{3+}$ from waste by dissolving the compounds in functionalized ionic liquid followed by precipitation stripping with oxalic acid.[14] After calcination, a recovered red lamp phosphor was obtained with identical quality as the original. This
35 method is particularly efficient when the europium concentration in the waste is constant. Unfortunately, this is not often the case. Therefore, complementary techniques have to be developed for

the recovery of europium and yttrium from rare earth mixtures. Separation of mixtures of rare earths by conventional methods
40 (e.g. solvent extraction, ion exchange) is a time-consuming and expensive procedure due to the very similar chemical properties of these elements, which all occur in a stable trivalent oxidation state.[15] However, since europium can easily be reduced to its divalent state, it can be removed from a mixture of rare-earth
45 elements more efficiently by a selective reduction technique.[16] This reduction of Eu(III) to Eu(II) is typically done chemically by zinc powder or zinc amalgam,[17-23] electrochemically by graphite or titanium electrodes [24-30] or photochemically by using excimer lasers or (high or low pressure) mercury lamps.[31-43] Chemical
50 reduction with zinc causes contamination of the rare-earth solution by Zn(II) ions and the use of zinc amalgam involves the risk of mercury pollution. The current efficiency of electrochemical reduction of Eu(III) in aqueous solutions is low due to the evolution of hydrogen gas.[44] In this paper,
55 photochemical reduction is used, since less toxic and harmful

chemicals are consumed and the best selectivity is obtained.[45-49] This technique introduces photons to the medium, emitted by a light source, that assist in the electron transfer of an electron from the solvent to the europium ion, causing the reduction of Eu(III) to Eu(II). Two decades ago, first photochemical experiments on rare earths were conducted. However, the light sources in these studies were lasers, which are expensive and difficult to operate, and the sample volumes were limited to several millilitres. Furthermore, the economic importance of rare earths has skyrocketed in the past couple of years, and created a boost for rare earth recycling research. The photochemical recovery of europium from binary Eu/Y mixtures is studied, since this couple of rare earths is found in waste streams of lamp phosphors. The performance of isopropanol as a scavenger, a less toxic compound than the commonly used scavenger formic acid, is examined. In particular the pH dependence of the separation and the use of realistic binary Eu/Y mixtures is investigated. Commercial rare earth mixtures are synthetically mimicked to study the possibility of europium recycling in lamp phosphor waste streams. In these phosphors, up to 10 at. % of europium is substituted into the yttria (Y_2O_3) host lattice. In principle, it is possible to go up to 50 at. % of europium but due to the high price of europium this is economically not viable. Less than 3 at. % on the other hand will reduce the efficiency of the lamps phosphor since the tail of the charge-transfer band will not be able to absorb all the UV radiation of 254 nm emitted by the mercury atoms in the fluorescent lamp.[50] Hence, next to equimolar Eu/Y mixtures, molar ratios between 1/10 and 1/20 are tested.

Theoretical background

Photochemical reduction of europium occurs when a mixture containing trivalent europium ions is illuminated. During this process, an electron from the ligand is transferred to the europium ion and Eu(III) is reduced to Eu(II). In aqueous solutions, a charge-transfer band (CT band) from water to europium is located at 188 nm (Eq. 1).[39] Low-pressure mercury lamps (LPMLs) have their main spectral output at 185 nm and 254 nm and hence they are suitable light sources for selective photochemical reduction of europium.

$$[Eu(H_2O)_n]^{3+} \xrightarrow{188\,nm} [Eu(H_2O)_{n-1}]^{2+} + OH^{\cdot} + H^+ \qquad (1)$$
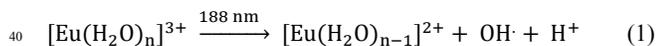
A reverse photochemical process, i.e. photochemical oxidation of Eu(II) to Eu(III), can occur when radiation of 366 nm is applied. Eu(II) has a 4f-5d transition which causes the loss of an electron according to Eq. 2:[51]

$$2\,Eu^{2+} + 2\,H^+ \xrightarrow{366\,nm} 2\,Eu^{3+} + H_2 \qquad (2)$$
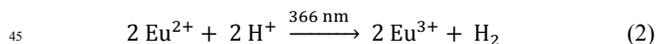
Several measures can be taken to maximize the yield of divalent europium. First of all, the reduced species has to be removed from the solution in order to avoid photochemical re-oxidation or reactions with the hydroxyl radicals. This can be done by adding a selective precipitating agent such as sulfates. Trivalent rare earth sulfates are much more soluble than europium(II) sulfate: europium(II) sulfate has a solubility of 0.001 g / 100 g H_2O, much lower than europium(III) sulfate (2.10 g / 100 g H_2O) and yttrium(III) sulfate (7.47 g / 100 g H_2O).[52] Therefore, only the
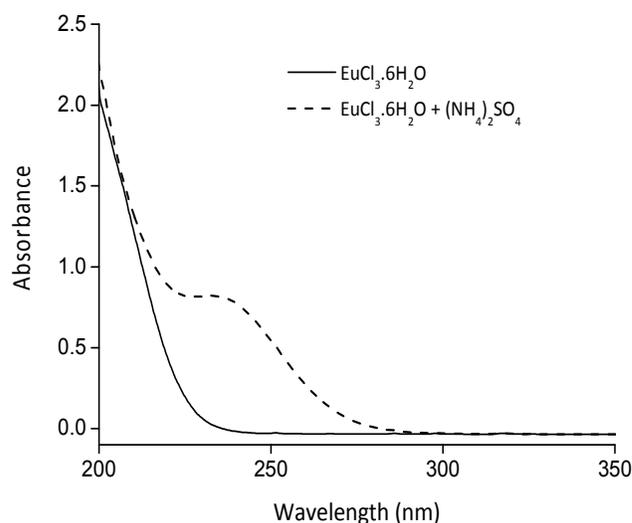
Fig. 1 UV/Vis spectrum of EuCl$_3$·6H$_2$O with and without the presence of ammonium sulfate (pH 1 solution).

reduced species will be removed from the solution as EuSO$_4$. Possible sulfate sources are ammonium sulfate, potassium sulfate and sulfuric acid. It should be noted that the presence of sulfate ions generates an additional reducing effect, namely in a CT band from sulfate to europium(III) at 240 nm (Eq. 5 and Eq. 6).[39] The CT band of the europium(III) sulfate complex occurs at lower energy than the europium(III) aquo complex and can be visualized on a UV/Vis spectrum (Figure 1).

$$SO_4^{2-} \xrightarrow{240\,nm} O^{\cdot}SO_3^- + e^- \qquad (5)$$

$$Eu^{3+} + e^- \rightarrow Eu^{2+} \qquad (6)$$
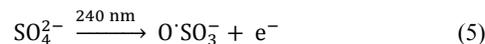
The formed O$^{\cdot}$SO$_3$ radical can further react with water according to Eq. 7, and the hydroxyl radicals are scavenged as explained in Eq. 9 (see later).

$$O^{\cdot}SO_3^- + H_2O \rightarrow HSO_4^- + OH^{\cdot} \qquad (7)$$
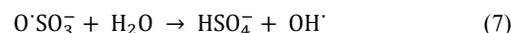
Since a low-pressure mercury lamp (LPML) has an intense band at 254 nm, this CT band is also exploited. The sulfate concentration will determine the maximum removal of europium, since a small fraction of EuSO$_4$ will remain in solution according to the solubility product of europium(II) sulfate (Eq. 8).[52]

$$Eu^{2+} + SO_4^{2-} \rightleftharpoons EuSO_{4,s} \qquad K_{sp} = 1.5 \cdot 10^{-9} \qquad (8)$$

A large excess of sulfate will reduce the equilibrium concentration of divalent europium and therefore shift the equilibrium to the precipitate. De Morais and Ciminelli studied this influence and observed an optimal sulfate/europium molar ratio of 7/1, although the impact of shifting to slightly lower ratios is very limited.[43] In this study, a sulfate/europium ratio of 5/1 was chosen.

Secondly, the reactive hydroxyl radicals formed in Eq. 1 have to be removed, since they can react with Eu(II) and consequently oxidize it back to Eu(III). Scavengers are, therefore, added to the reaction medium, which destroy the OH$^{\cdot}$-radicals and form more stable organic radicals. Typical scavengers are organic compounds such alcohols, esters or carboxylic acids and the general reaction is shown in Eq. 9. Commonly used scavengers

are formic acid and isopropanol.[29,39-43]

$$R_3CH \xrightarrow{\cdot OH} R_3C \cdot + H_2O \qquad (9)$$
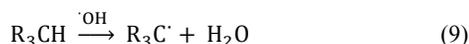
The formed organic radicals can induce an extra reduction of trivalent europium, as described in Eq. 10 for formic acid and Eq.
5 11 for isopropanol.

$$C \cdot OOH + Eu^{3+} \rightarrow Eu^{2+} + CO_2 + H^+ \qquad (10)$$

$$(CH_3)_2C \cdot OH + Eu^{3+} \rightarrow Eu^{2+} + (CH_3)_2CO + H^+ \qquad (11)$$
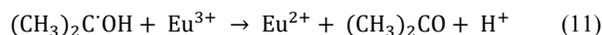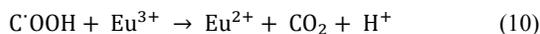
The use of formic acid speeds up the reduction reaction, due to an additional photo-assisted reduction process. At 260 nm, formic
10 acid splits up in a ·COOH-radical (Eq. 12) that can induce a reduction of Eu(III) (see Eq. 10). The scavenger activity of HCOOH is not compromised by this photo-assisted reduction of Eu(III), since H· can act as a radical scavenger for OH·-radicals as well. The hydrogen radicals can also recombine to form H_2.
15 The reactions are displayed in Eq. 13 and Eq. 14. High scavenger requirements are needed, with a scavenger/europium molar ratio of 500/1.[43]

$$HCOOH \xrightarrow{260 \text{ nm}} C \cdot OOH + H \cdot \qquad (12)$$

$$H \cdot + OH \cdot \rightarrow H_2O \qquad (13)$$

20 $$2 \, H \cdot \rightarrow H_2 \qquad (14)$$
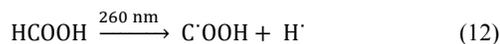
Another important factor is the acidity of the reaction medium. From Eq. 1, it is evident that protons are formed during the photochemical reduction of Eu(III). On the other hand, protons are consumed by the photochemical back reaction (Eq. 2).
25 Therefore, a low proton concentration and hence higher pH is desirable. Furthermore, Eu(II) is thermodynamically more stable in less acidic conditions, as determined in the Nernst equation (Eq. 15, and simplified at standard conditions (T = 298 K, p = 1 atm, Eq. 16)). This expression determines the pH-dependence of
30 water stability.

$$E_{H^+/H_2} = E^0_{H^+/H_2} + \frac{RT}{nF} \ln\left(\frac{[H^+]^2}{p_{H_2}}\right) \qquad (15)$$

$$E = -0.059 \, pH \qquad (16)$$

The standard redox potential of Eu(III)/Eu(II) in water is -0.34V.[53] From Eq. 17, it can be calculated that Eu(II) is
35 thermodynamically stable in water above pH 5.8. Kinetically, Eu(II) is temporarily stable at lower pH as well, but higher pH is favored. However, too alkaline conditions (pH > 6.8) will lead to hydrolysis of europium and subsequent precipitation of Eu(OH)$_3$. Since all rare earths undergo hydrolysis at these pH values and
40 metal concentration, no selective removal of europium can be achieved.[43,54,55] Therefore, an optimum pH will be reached between pH 0 and pH 6.
A last measure to optimize europium reduction is the use of a light source which only emits light that triggers the reduction of
45 europium, i.e. light of 188 nm (water-to-europium CT band) and 240 nm (sulfate-to-europium CT band). Light of 366 nm should be avoided, since this triggers the photochemical oxidation of divalent europium. From the irradiance profile of the LPML used in this study, it is seen that the main spectral output is located
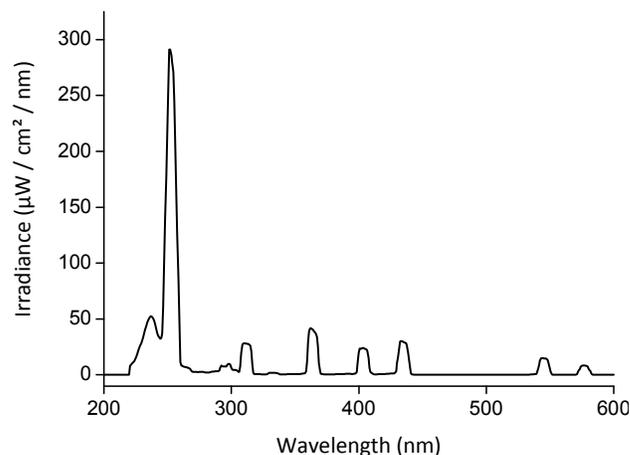
50 **Fig. 2** Irradiance output of U-shaped 11W LPML.

around 250 nm (Figure 2). The output below 200 nm could not be visualized, but there is also an intense band around 185 nm. Less dominant emission peaks above 300 nm are observed as well.
55 Around 366 nm, a weak output is seen. This band is far less intense than the high emissions related to the forward (reduction) reaction. However, the extinction coefficient of the Eu(II) f-d transition is much higher than that of the CT bands.[51] Hence, a considerable loss in efficiency is expected due to the
60 polychromatic nature of LPMLs.
To summarize, key parameters in the photochemical reduction of europium are the concentration of sulfate, the type and concentration of scavenger, the pH and the used light source. Next to that, the rare earth composition is an important factor.
65 Equimolar, binary rare-earth mixtures do not reflect actual waste streams. Therefore, more realistic mixtures with different molar ratios (based on applications) are studied.

Experimental

Chemicals

70 The rare earths (europium and yttrium) were added as chloride hexahydrate salts (LnCl$_3$·6H$_2$O) and have a purity of 99.9% (Acros Organics). Ammonium sulfate (99.6 %, Acros Organics) was added in its solid form. Scavengers formic acid (99.9%, ChemLab) and isopropanol (99.5 %, VWR) were introduced as
75 liquids. Red lamp phosphor powder (Y$_2$O$_3$:Eu^{3+}, Nichia Japan) was added as solid particles.

Light source

For all experiments, a U-shaped 11W low-pressure mercury lamp (LPML) (TL-S, Philips) was used with an arc length of 21 cm.
80 The spectral output shows maxima at 185 nm and 254 nm and the irradiance profile is shown in Figure 2. Note that output below 200 nm could not be visualized with the analyzing equipment, hence the band at 185 nm is not shown.

Experimental preparation and set-up

85 An aqueous HCl solution was prepared by diluting a 1M HCl stock solution with MilliQ water to obtain the desired pH. Subsequently, the correct amount of the rare-earth chloride hexahydrates and ammonium sulfate was added to 250 mL of the aqueous solution. Immediately prior to illumination, 20 vol% (50
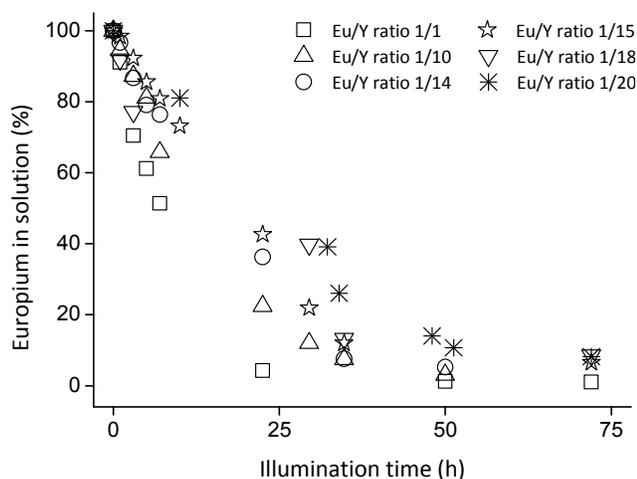
Fig. 3 Comparison of different Eu/Y molar ratios. Conditions: pH 1.2, volume = 250 mL, 20 vol% (50 mL)) formic acid scavenger, 10 mM EuCl$_3$·6H$_2$O, 50 mM (NH$_4$)$_2$SO$_4$, varying concentrations of YCl$_3$·6H$_2$O to obtain indicated Eu/Y ratio (See Table 1).

Fig.4 Separation of Eu/Gd with a molar ratio of 1/30. Conditions: 250 mL pH 1 solution; 10 mM EuCl$_3$·6H$_2$O, 300 mM GdCl$_3$.6H$_2$O, 50 mM (NH$_4$)$_2$SO$_4$; 20 vol% (50 mL) HCOOH

mL) of the scavenger (formic acid or isopropanol) was mixed with the rare-earth solution. The sample solution was poured into a 1L glass reaction vessel and placed on a stirring plate. The U-shaped 11W LPML was immersed into the solution and the light source is switched on. Samples were taken at regular time intervals to determine the rare earth concentration in solution.

To protect the environment from the hazardous UV radiation of the lamps, experiments were carried out in a sealed dark box. Special UV protective goggles (LOT-QuantumDesign) were worn during the experiments.

1.5 g of red lamp phosphor powder was dissolved in 250 mL of a 0.5 M HCl solution. 50 mM (NH$_4$)$_2$SO$_4$ was added and the pH was altered to 3.9 by adding drops of 1 M NaOH. 20 vol % of isopropanol scavenger was added. The solution was illuminated with the same 11 W LPML for 50 hours.

Analysis equipment

The UV/Vis-spectra were taken on a Shimadzu UV1601 in an optical range of 190 nm to 1100 nm. Diluted samples were prepared and analyzed in quartz cuvettes.

The metal concentration of the liquid phase was measured by total-reflection X-ray fluorescence (TXRF) spectrometry, using a Bruker S2 Picofox TXRF spectrometer. 100 µL of the sample was mixed with 100 µL of a 1000 mg/L gallium internal standard solution and diluted with 800 µL MilliQ-water, and a droplet of 10 µL was put on a quartz sample carrier. The sample carrier was precoated with a silicone solution in isopropanol (SERVA) to make the carrier hydrophobic in order to avoid spreading of the sample droplet of the carrier. The quartz glasses were dried in an oven at 60 °C for 30 min and analyzed with the TXRF spectrometer. After reaching the final illumination time, the precipitate was isolated by filtration. A fraction of the precipitate was redissolved in a concentrated HCl solution and analyzed with TXRF to determine the purity.

The spectral output of the LPML was measured using a QE65 Pro Scientific Irradiance meter (Ocean Optics) at a distance of 3 cm from the light source. The irradiance meter was calibrated by a DH-2000 calibration light source (Ocean Optics) for a spectral region between 200 and 900 nm.
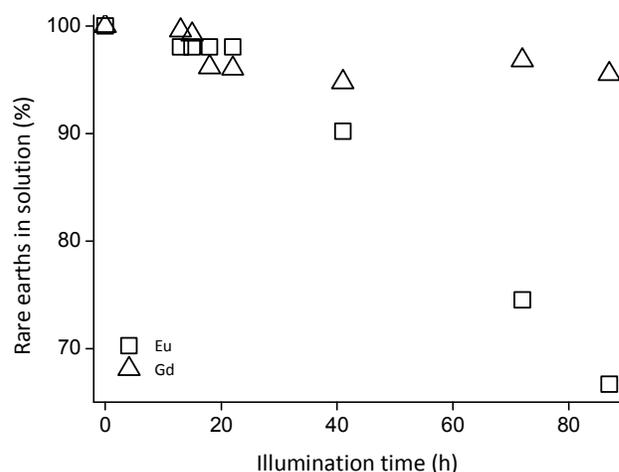
Results and discussion

In this work, emphasis is put on Eu/Y mixtures from lamp phosphors. Europium is recycled from mimicked commercial Eu/Y mixtures that can be found in lamp phosphor waste streams. Therefore, molar ratios are varied between 1/10 (10 at.%) and 1/20 (5 at.%). Table 1 gives an overview of the investigated molar ratios. The results for Eu removal from the molar ratio experiments are graphically summarized in Figure 3.

Table 1 Molar ratios of investigated Eu/Y mixtures

Eu/Y ratio	[Eu^{3+}] (mM)	[Y^{3+}] (mM)
1/1	10	10
1/10	10	100
1/14	10	140
1/15	10	150
1/18	10	180
1/20	10	200

Less than 2 % of yttrium removal was observed in all samples, and redissolution of the precipitates indicates a europium purity of 98.5 %. Therefore, the yttrium concentration is not shown on the graph. It is seen that an increasing excess of yttrium clearly delays the europium precipitation, and longer illumination times need to be applied to reach the same percentage of removal. However, all mixtures converge to the same removal percentage of > 90 %. The excess of yttrium has a kinetic effect on the reaction. This could be explained by the fact that yttrium occupies sulfate ions in its second coordination sphere. Therefore, with a higher yttrium concentration it is less likely for a europium ion to meet a sulfate ion. The excess of yttrium diminishes the amount of available sulfate ions for electron transfer and precipitation. The high yttrium concentration only provokes a slower removal rate, but sufficient illumination time does make it possible to recover europium. This is in contradiction with earlier studies where an excess of gadolinium prohibited europium removal for a molar ratio of Eu/Gd = 1/27.[43] The applied illumination time of 4 hours was in that study not long enough to enable europium precipitation. To make sure that the use of
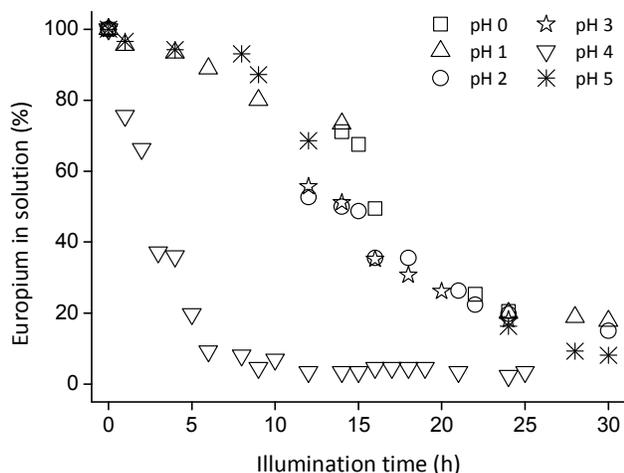
Fig.5 Influence of the pH on the illumination for the separation of equimolar Eu/Y mixtures. Conditions: 250 mL pH 0-5-solution; 10 mM EuCl$_3$6H$_2$O, 10 mM YCl$_3$·6H$_2$O, 50 mM (NH$_4$)$_2$SO$_4$; 20 vol% (50 mL) isopropanol scavenger.
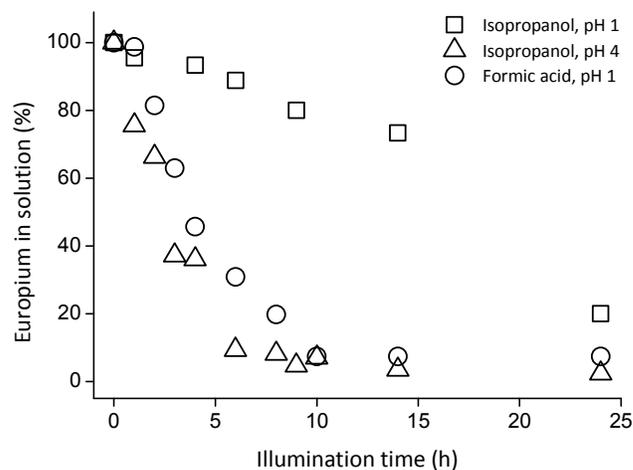
Fig.6 Comparison of formic acid and isopropanol scavenger at pH 1 and pH 4 (only for isopropanol). Conditions: volume = 250 mL, 10 mM EuCl$_3$·6H$_2$O, 10 mM YCl$_3$·6H$_2$O and 50 mM (NH$_4$)$_2$SO$_4$, 20 vol% (50 mL) scavenger (formic acid or isopropanol).

yttrium or gadolinium has no influence, since the photochemical reaction is selective for europium, a europium/gadolinium-mixture with a molar ratio of 1/30 was tested. The results are graphically depicted in Figure 4. It is seen that europium can be removed from the mixture with an excess of gadolinium.

However, removal only starts after 30 hours and doesn't reach the same efficiency as in the yttrium experiment. This can be explained by the fact that the excess of gadolinium is higher than that of yttrium, and that gadolinium has some weak f-f absorptions between 200 and 350 nm, the wavelength region of the photochemical reduction of europium.[56-58] Nevertheless, europium could be removed selectively and the precipitate had a 96 % europium purity.

In the previous experiments, formic acid was used as a scavenger because of the extra photo-assisted reduction of europium via the organic radical (see Eq. 10 and Eq. 12). However, two major drawbacks are associated with this scavenger. First of all, formic acid is a hazardous compound and a fairly large amount is consumed during the reaction. Secondly, the strong acidity forces us to work at very low pH values (pH 0-1). This is disadvantageous since the formation of divalent europium is thermodynamically disfavoured below a pH of 5). Isopropanol on the other hand is less harmful for the environment [59,60] and more importantly does not alter the pH of the aqueous solution.[61] Being able to operate at higher pH will counter the lack of extra photo-assisted reduction ability. A disadvantage of isopropanol is the low dielectric constant. A decrease of the dielectric constant of the mixture will lower the solubility of trivalent rare-earth sulfates and therefore limits the total rare-earth concentration in the feed solution. This is known as the anti-solvent effect, and leads to non-selective precipitation of all rare earths even in the absence of light.[41,62,63] Dark experiments of all mixtures were performed simultaneously with the illumination experiment, to make sure the precipitation was due the irradiation and did not occur in the absence of light.

The pH of the mixtures was measured before and after scavenger addition, and this pointed out that isopropanol did not significantly change the pH of the medium. As expected, the reaction rate was enhanced by increasing the pH of the solution up to a pH of 6 at which hydrolysis of rare earths occurs and both trivalent europium and yttrium precipitate non-selectively. Previous studies mention there is no influence of the pH, but since these experiments were carried out with formic acid the pH-range was only varied from 0.3-1.5.[42,43] When higher pH values were considered, it was observed that at higher pH values the same europium removal is reached for significantly shorter illumination times (Figure 5). Starting from pH 6, hydrolysis and subsequent precipitation of Eu(OH)$_3$ and Y(OH)$_3$ were observed. The europium concentration decreased faster than the yttrium concentration, since a fraction of the europium ions still underwent the photochemical reduction followed by precipitation as EuSO$_4$. However, no efficient separation from yttrium could be obtained due to hydrolysis. Dark experiments confirmed co-precipitation of yttrium and europium, proving that this is a result of the chemical environment and not due to illumination.

The equimolar mixture was also tested with formic acid as a scavenger and compared to the isopropanol experiments. The result is shown in figure 6. It is seen that the formic acid scavenger works much faster than the isopropanol scavenger at pH 1. However, at pH 4 the isopropanol system shows better performance. Since formic acid solutions cannot reach this pH value, the removal rate cannot be improved by changing the pH. This result clearly indicates that isopropanol is in fact a better choice of scavenger. The reaction conditions are milder, the hazardous formic acid can be substituted for the less harmful isopropanol and the illumination time can be reduced to obtain the same europium removal: 90 % of removal is achieved after 6 hours for pH 4 with isopropanol and after 8 hours for the formic acid mixture at pH 1. The purity of the precipitated EuSO$_4$ is not compromised (98.5 %) and the efficiency of removal is maintained at 98 %. Please note that in these experiments, the scavenger volume is kept constant. Since isopropanol has a higher molar mass and a lower density than formic acid, the isopropanol/europium molar ratio (260/1) is lower than the formic acid/europium molar ratio (530/1). Hence, isopropanol shows a better performance with a lower scavenger requirement and clearly is a better alternative than the formic acid scavenger.
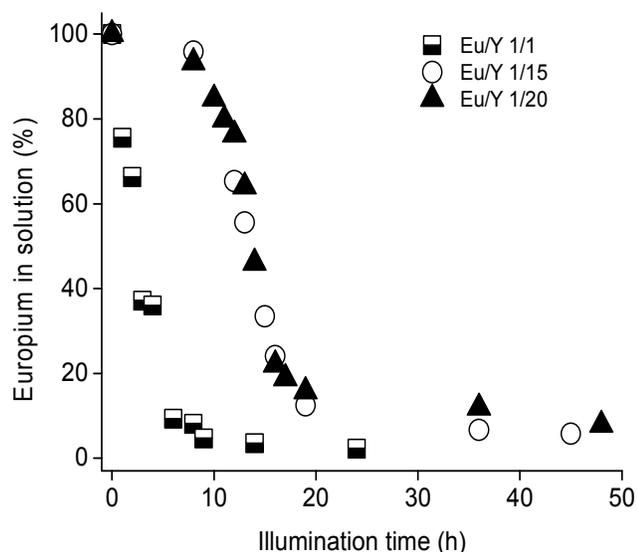
Fig. 7 Comparison of different Eu/Y molar ratio (1:1, 1:15 and 1:20). Conditions: 250 mL of a pH 4.5 solution with 10 mM $EuCl_3 \cdot 6H_2O$, 50 mM $(NH_4)_2SO_4$ and 150 mM (1:15 ratio) or 200 mM (1:20 ratio) $YCl_3 \cdot 6H_2O$, 20 vol% (50 mL) isopropanol scavenger.
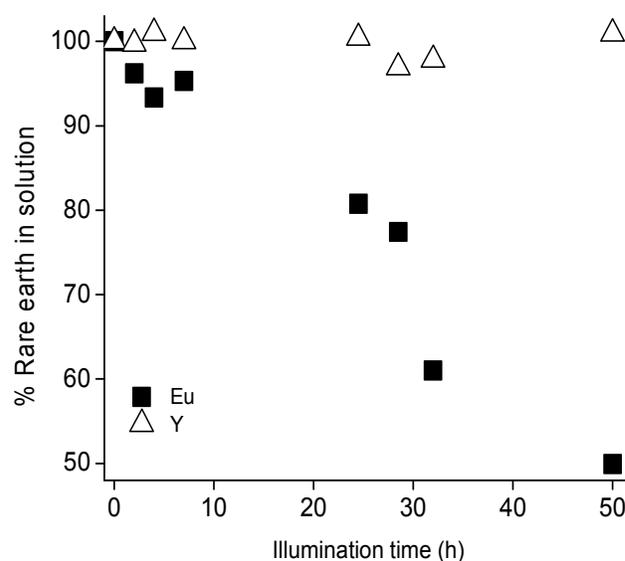
Fig. 8 Separation of europium and yttrium from industrial YOX powder. Conditions: 250 mL of a pH 3.9 solution with 6 g/L YOX powder (Eu/Y 1/30), 50 mM $(NH_4)SO_4$, 20 vol% (50 mL) isopropanol scavenger.

Therefore, isopropanol is used in experiments with varying molar ratios, to determine whether isopropanol can achieve better removal rates of europium for realistic binary mixtures of europium and yttrium. Molar Eu/Y-ratios of 1/15 and 1/20 are examined at pH 4.5, since this is the optimal condition for isopropanol. The results are depicted in Figure 7, with the Eu/Y 1/1 ratio as a reference. Approximately 90 % of the europium ions were removed from the solution. The maximal removal of yttrium, in the last sample at 48 hours of illumination, was less than 5 %. Analysis showed a purity of 98.5 %, with 1.5 % of yttrium impurity due to co-precipitation. All dark experiments showed no change in europium or yttrium concentration. Compared to the same experiment with the formic acid scavenger, faster europium removal is observed: for the 1/15 ratio, 88 % of removal is obtained after 19 hours with isopropanol and only after 35 hours with formic acid, almost a double illumination time. For the 1/20 ratio, 89 % of europium is removed after 40 hours with isopropanol, and only after 51 hours with formic acid (or 20 % more). Shorter illumination times are hence needed for the same amount of removal and purity of the precipitate.

For the best system with 20 vol% isopropanol at a pH around 4, the separation of europium and yttrium from real red lamp phosphor powder was tested. The result is shown in Figure 8. For a Eu/Y ratio of 1/30, it is seen that 50 % of the europium is removed after 50 hours of illumination. The $EuSO_4$ precipitate had a purity of 96 %. This experiment proves that the technique can be used to separate yttrium and europium from industrial lamp phosphors.

Conclusions

Photochemical reduction of europium and subsequent precipitation as $EuSO_4$ has proven to be a promising technique to selectively remove europium from aqueous rare-earth mixtures and shows great potential for the recovery of europium from red

lamp phosphor waste streams. Isopropanol is selected as scavenger to study the influence of the pH on the europium removal. Unlike formic acid, a commonly used but toxic and acidic scavenger, isopropanol allows to operate at higher pH a values. Moreover, lower scavenger requirements are needed when working with isopropanol compared to formic acid. Isopropanol shows better performance with only half the scavenger/europium molar ratio as compared to formic acid. Due to the better thermodynamic stability of Eu^{2+} at higher pH, faster europium removal is observed when increasing the pH. At pH 4, the optimum is reached and the removal rate is slightly faster than that of the formic acid systems operating at pH 0-1. Next to that, non-equimolar mixtures of europium and yttrium were tested to check whether europium could be recycled from commercial red phosphor waste streams. Eu/Y ratios ranging from 1/1 to 1/20 were studied. Experiments showed that europium recovery is slowed down due to the excess of yttrium. However, applying longer illumination times made it possible to selectively remove 90 % of europium with a purity of 98.5 %. Therefore, the excess of yttrium only induces a kinetic effect. For these mixtures, using isopropanol at a pH of 4.5 again showed significantly faster removal rates than when formic acid was added, without compromising the purity of the precipitate. For a Eu/Y ratio of 1/15, using isopropanol instead of formic acid almost halved the illumination time to achieve 88 % of europium removal. For a 1/20 ratio, 88 % of removal was obtained 20 % faster with isopropanol compared to formic acid. Europium from real red lamp phosphors was also obtained by dissolving industrial YOX powder and illuminating the solution for 50 hours. 50 % of europium was removed as $EuSO_4$ with a purity of 96 %. This proves that europium can be recovered from spent end-of-life red lamp phosphors.

Long illumination times are not desirable for commercial recycling, since residence times are long and hence continuous systems are not feasible. However, by using stronger (i.e. higher irradiances) and monochromatic (to suppress photochemical back reaction), the illumination time could be decreased

This method can be a promising pre-preprocessing step to efficiently recover all europium from rare earth mixtures, prior to subsequent separation of the other rare earths into pure fractions. Moreover, by efficiently recycling spent consumer goods, less rare earth mining is needed. Therefore, there is less overproduction of rare earth elements lower in demand on the market, solving the so-called balance problem.[64] Recycling of rare earths therefore solves the issue of criticality, and also provides ecological advantage.

Acknowledgements

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Textual abstract

A highly efficient and selective separation technique to remove europium from Eu/Y mixtures, in order to recycle europium from red lamp phosphors.
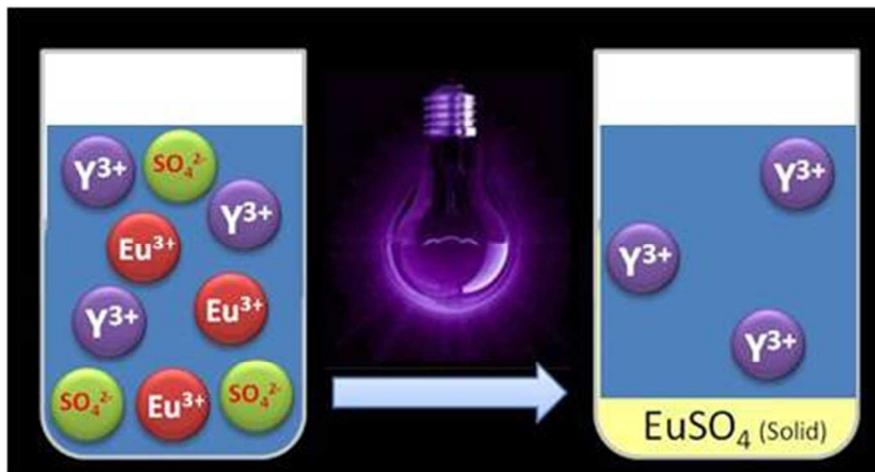
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