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Screening and selection of technologically applicable microorganisms for recovery of rare earth elements from fluorescent powder

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ABSTRACT

Rare Earth Elements (REE) are essential elements in many new technology products. Up to now, recycling is poorly established and no environmentally friendly strategies are applied. Modern biotechnologies like bioleaching can contribute to overcome the current limitations. In this study, we investigated bioleaching approaches exemplary for fluorescent phosphor (FP), which is accumulated during the recycling of fluorescent tubes and energy saving bulbs. A broad spectrum of different microorganisms were tested regarding their potential to leach REE from FP. Among them were classical acidophilic microorganisms, as well as various heterotrophic ones, producing organic acids or metal complexing metabolites, or having a high metal tolerance. Larger amounts of REE were leached with the strains *Komagataeibacter xylinus*, *Lactobacillus casei,* and *Yarrowia lipolytica*. Besides the COOH-functionality, also other biotic processes contribute to metal leaching, as comparison with indirect leaching approaches showed. Among the different REE components of the FP preferably the oxidic red dye yttrium europium oxide (YOE) that contain the critical REE yttrium and europium was leached. The results provide the basis for the development of an environmentally friendly recycling process for REE from waste materials.

1. Introduction

Rare Earth Elements (REE) are assigned to the group of critical raw materials (European, 2014). They are a part of nearly all new technologies (e. g. computer flat screens and lasers, as well as highly effective magnets for wind mills, and electric cars) (Schüler et al., 2011). Nevertheless, the end-of-life recycling-rates for REE are still less than one percent (Reck and Graedel, 2012). Currently, about 175 tons of REE containing fluorescent phosphor (FP) from fluorescent bulbs and energy saving bulbs are yearly accumulated in Germany (Gallenkemper and Breer, 2012, Riemann, 2014). Keeping in mind that FP contains about ten percent of REE-oxides (Haucke et al., 2011), it can be estimated that these compounds account for one percent of the REE imports to Germany (Schüler et al., 2011). Despite the increasing application of LEDs, there are still considerable amounts of compact fluorescent lamps in circulation, and moreover, during the last years huge amounts were stored. Besides, also LEDs contain fluorescent phosphors, although the amounts are smaller (Lim et al., 2013). To our knowledge, there is no existing industrial recycling process for waste FP, even though there are many studies about possible strategies. These approaches use strong inorganic acids or toxic chemicals (Tanaka et al., 2013).

Bioleaching methods are environmentally friendly alternatives to classical approaches. In contrast to conventional leaching methods that require a constant influx of reagents, in case of bioleaching the agents are directly produced in the system (Beolchini et al., 2012). For these processes there are basically two strategies: At first, the classical bioleaching with acidophilic microorganisms as it is industrially used for copper leaching and has been used also for the bioleaching of electronic scrap (Brandl et al., 2001). These processes require an acidic pH-value as well as iron or sulfuric compounds that are oxidized by the microorganisms. The produced sulfuric acid works as leaching agent. However, these compounds are not part of REE-waste. The other option is to use chemoorgano-heterotrophic microorganisms that mobilize metals

Abbreviations: BAM, Barium Magnesium Aluminate; CAT, Cerium Magnesium Aluminate; CBT, Cer-Gadolinium Magnesium Pentaborate; FP, fluorescent phosphor; HP, Halophosphate; HPLC, High Pressure Liquid Chromatography; *K. xylinus*, *Komagataeibacter xylinus*; *L. casei*, *Lactobacillus casei*; LAP, Lanthanum Phosphate; REE, Rare Earth Elements; XRD, X-ray diffraction analysis; XRF, X-ray fluorescence analysis; *Y. lipolytica*, *Yarrowia lipolytica*; YOE, Yttrium Europium Oxide.

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mainly by the produced metabolites (Bosecker, 1997, Krebs et al., 1997). Possible metabolites are metal-binding molecules like siderophores (Fe) and chalkophores (Cu), which can unspecifically bind also other metal ions (Emmanuel et al., 2011). Furthermore, organic acids have a high potential to leach REE (Goyne et al., 2010). Besides the effect of acids, which mobilize the REE-containing phosphor dyes, the leaching process is also influenced by complexation by removing the REE from the chemical equilibrium (Goyne et al., 2010). An advantage of this process is the tolerance of a broader pH-range by the used microorganisms, as well as the possibility to use cheap nutrients like molasses or glycerin (Bosecker, 1997, Krebs et al., 1997). Other strategies based on oxidative or reductive processes are not applicable in case of FP, because the REE in FP are already at highest oxidation state, therefore further oxidation is not possible. On the other hand, reduction is impossible as the redox potential of REE is strongly negative compared to other elements, thus the REE cannot serve as electron acceptor (Morss, 1985).

The recovery of metals from anthropogenic wastes by bioleaching was investigated in several publications during the last years. In an early publication Krebs et al. (1997) summarized leaching experiments from different metal containing material with various microorganisms and their metabolic products. Several studies used chemolitho-autotrophic bacteria like *Acidithiobacillus ferrooxidans* and *A. thiooxidans* as well as *Leptospirillum ferrooxidans* for leaching of waste materials, for example electronic scrap or fluorescent powders at aerobic conditions (oxidative leaching) (Brandl et al., 2001; Zhu et al., 2011; Beolchini et al., 2012). However, there are also many examples for the application of chemoorgano-heterotrophic microorganisms such as *Aspergillus niger*, *Penicillium simplicissimum*, or *Yarrowia lipolytica*, always connected with a production of organic acids (Talasova et al., 1995; Bosshard et al., 1996; Brandl et al., 2001). These organisms were successfully used for the extraction of metals from waste materials such as red mud, fly ash, or electronic scrap.

Regarding REE, many publications investigated minerals. Most studies concentrated on monazite, which is a REE containing phosphate mineral. In most of these studies different organic acids that were produced by various microorganisms were used as leaching agents (Hassanien et al., 2013; Shin et al., 2015; Maes et al., 2017). Other researchers proved that a mobilization of REE can be mediated by siderophores (Bau et al., 2013). All these studies indicated the significance of microbial metabolites such as organic acids and siderophores for the biogeochemistry of REE.

Only few studies describe the microbial mobilization of REE from secondary resources. Most recently we used the "tea fungus" Kombucha, a symbiotic microbial consortium that is usually used for fermentation of tea and well known for the production of many different organic acids, for the extraction of REE from FP (Hopfe et al., 2017). In this study, the FP was incorporated into the cellulosic pellicle during the leaching approach. The accessibility of the FP for the produced cellular metabolites and consequently their application was limited. Furthermore, leaching efficiency was too low for a technical application. Another recent study used *Gluconobacter oxydans* that produced gluconic acid for the extraction of REE from spent fluid cracking catalysts (FCC) (Reed et al., 2016).

In summary, various articles demonstrate the principal ability of different microorganisms to leach anthropogenic waste products, but only few studies consider REE containing wastes. On the other hand, many studies describe microbial mobilization of REE from ores suggesting that it should be possible to leach REE also from secondary resources. In these studies, mainly organic acids, but also metal chelating molecules such as siderophores were identified as responsible agents. Therefore, in the present study several microorganisms producing various organic acids were selected and investigated regarding their ability to leach REE from spent FP. Results were compared with the usage of "classical" chemolitho-autothropic bacteria as control.

2. Material and methods

2.1. Fluorescent phosphor

Spent FP was provided by Larec Lampen-Recycling Gesellschaft mbH (Germany). FP of the same batch as described in Hopfe et al. (2017) was splitted in amounts of 0.85 g and treated as previously described. The elemental composition of the FP was determined in detail in Hopfe et al. (2017) by X-ray fluorescence analysis (XRF). These data were used in the present study as reference values. Furthermore, X-ray diffraction analysis (XRD) was used for determination of the single compounds of FP. A PANalytical EMPYREAN θ-θ diffractometer in a continuous step mode from 5 to 80°2 θ with a step width of 0.016°2 θ and a total time of 2 h and 4 min was used. The device was equipped with a Co tube (operating at 35 kV and 35 mA) and a Fe filter, a X'Celerator solid state strip detector (using 64 of 128 channels), an automatic divergence slit, and a 15 mm beam mask, for a constant irradiated area of 10 to 15 mm^2. The amount of glass in the FP was estimated by visualizing with phase-contrast microscope.

2.2. Microorganisms and cultivation

Microorganisms were selected based on leaching data given in literature e. g. Krebs et al. (1997) and Shin et al. (2015). Depending on the microbial strain and the envisaged metabolites, the microorganisms were cultured on different media that were optimal for the respective strain as described in literature. Detailed information on media composition are listed in Table S1 of supplementary material. *Acidithiobacillus ferrooxidans* DSM-No: 14882 and *Acidithiobacillus thiooxidans* DSM-No: 14887 were chosen as representatives for chemolitho-autotrophic acidophilic bacteria. Cultivation and bioleaching experiments were performed at aerobic conditions (oxidative bioleaching) as described in other studies investigating the bioleaching of electronic scrap. All other selected microorganisms belong to the group of chemoorgano-heterotrophs: *Bacillus licheniformis* DSM-No: 8785 (production of polyglutamic acid), *Burkholderia glumae* DSM-No: 9512 (production of oxalic acid), *Corynebacterium callunae* DSM-No: 20147 and *C. stationis* DSM-No: 20305 (production of glutamic acid), *Komatogateibacter xylinus* DSM-No: 2325 (strain of the mixed culture Kombucha), *Lactobacillus casei* DSM-No: 20011 (production of lactic acid), the yeasts *Priceomyces haplophilus* DSM-No: 70365 and *Yarrowia lipolytica* DSM-No: 3286 (production of citric acid), *Pseudomonas fluorescens* DSM-No: 50090 and a strain of our own lab collection (formation of the siderophore pyoverdine), *Streptomyces acidiscabies* (production of siderophores of hydroxamate type (Dimkpa et al., 2008)). *Lysinibacillus sphaericus* JG-A13, JG-B37 Iso 3, JG-B58, JG-B5T, and JG-C34 (isolates of a uranium mining waste pile, heavy metal tolerant, production of different organic acids and siderophores) (Selenska-Pobell et al., 1999).

2.3. Leaching experiments

The bioleaching experiments were performed as previously described (Hopfe et al., 2017). Accordingly, the microbial strains were precultured in the respective medium on a rotary shaker at 300 rpm at room temperature. 30 ml of the same medium containing 0.85 g of FP was inoculated with 1 ml of the preculture and cultured at the same conditions in 100 ml wide neck Erlenmeyer flasks for 14 days in a fume hood. As control, cultivation experiments without FP or without microorganisms were performed.