Recovery of zinc in phosphor wastes via electrokinetic treatments

M.Y. Yu\textsuperscript{a}, H. Paul Wang\textsuperscript{a,b,*}, C.Y. Chen\textsuperscript{a}, Tung-Li Hsiung\textsuperscript{a}, Yu-Ling Wei\textsuperscript{c}, H.-S. Tai\textsuperscript{d}, K.-C. Chiang\textsuperscript{b}

\textsuperscript{a} Department of Environmental Engineering, National Cheng Kung University, Tainan City, Taiwan
\textsuperscript{b} Sustainable Environment Research Center, National Cheng Kung University, Tainan City, Taiwan
\textsuperscript{c} Department of Environmental Science and Engineering, Tunghai University, Taichung City, Taiwan
\textsuperscript{d} Department of Safety, Health and Environmental Engineering, National Kaoshiung First University of Science and Technology, Kaoshiung, Taiwan

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Abstract

Speciation of zinc in phosphor wastes during electrokinetic treatments has been studied by in situ X-ray absorption near edge structure (XANES) spectroscopy in the present work. The least-square fits of the in situ XANES spectra show that the major zinc species in the phosphor waste are ZnS (77%), ZnO (10%), and Zn(OH)\textsubscript{2} (13%). During the electrokinetic treatment for 90 min, 25% of ZnS and 4% of ZnO are dissolved. About 42% of zinc is enriched on the cathode under the electric field (5 V/cm). Prolonging the electrokinetic treatment time to 4 h under the electric field of 5 V/cm, at least 80% of zinc in the phosphor waste can be recovered.

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1. Introduction

Zinc is generally used in illumination of the blue–green phosphor for field emission display (FED) [1]. Other luminescence phosphors have different colors such as ZnGa\textsubscript{2}O\textsubscript{4} (blue), ZnGa\textsubscript{2}O\textsubscript{4}:Mn\textsuperscript{2+} (green), ZnS:Ag:Cl (blue), and ZnS:Cu:Al (green) [2,3]. ZnO-based phosphors have a higher chemical stability in FED applications if compared with ZnS. Polystyrol, polyacrylate, polypropylene, or other polymers and alkaline silicates may be coated on the phosphors [4]. These coating materials enhance not only the emission intensity but also the electrical conductivity of phosphors. However, a large amount of phosphor wastes discharged from disassembling of TV, monitor and FEDs is to be effectively treated. In general, disposal of phosphor wastes in landfill sites may cause contamination problems in soils or groundwater. It is of great importance to develop effective methods for treatments of the phosphor wastes with recycling of valuable metals therein.

X-ray absorption near edge structure (XANES) spectroscopy uses a single-ion probe that can analyze select elements in a complex matrix. Furthermore, X-ray absorption by an ion is almost directly proportional to its concentration. Note that basic understanding at the molecular scale is of great importance and interest in the management of toxic elements in the waste. We have developed an electrokinetic method for recycling of valuable metals in the phosphor waste [5]. However, chemical structure of select elements and reaction path during the electrokinetic process are still not well understood. Under electric field, select elements may be migrated and enriched at electrodes [5]. Thus, the main objective of this work was to study speciation of zinc in the phosphor wastes during electrokinetic treatments by in situ XANES spectroscopy to reveal the feasible route for recycling of zinc from the phosphor wastes.

2. Experimental

The in situ XANES cell for electrokinetic remediation (EKR) experiments is shown in Fig. 1. The cell includes five main components: two Pt electrodes, two electrode reservoirs, a power supply, a cation exchange membrane (Nafion® 417, Aldrich) (to prevent precipitation of zinc hydroxides on the electrode) and films. The phosphor wastes (provided by television dismantle and recycling companies in Taiwan) were dried over night and ground in a mortar and sieved with a 2-mm screen. About 50 g of the phosphor wastes were filled in the cell and saturated...
with 0.01 M potassium nitrate as a conductive solution. During electrokinetic treatments, a 5 V/cm direct current was applied across electrode pairs. Concentration of zinc was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, JOBIN YVON model JY32/38).

In situ X-ray absorption spectra of zinc were determined near the anode (1.5 cm). The in situ Zn K-edge (9659 eV) XANES spectra were collected on the Wiggler BL17C at the Taiwan Synchrotron Radiation Research Center (SRRC). The electron storage ring operated at an energy of 1.5 GeV (current of 80–200 mA). A Si(1 1 1) double-crystal monochromator was used for selection of energy with an energy resolution of $1.9 \times 10^{-4}$. The X-ray absorption spectra were recorded using a fluorescence detector (Lytle detector) and the photon energy was calibrated by characteristic preedge peaks in the adsorption of Zn foil (9659 eV). The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. The absorption edge was determined at the half-height (precisely determined by the derivative) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum post-edge intensity. Semi-quantitative analyses of the edge spectra were conducted by the least-square fitting of linear combinations of standard spectra (such as ZnO, ZnS, and Zn(OH)$_2$) to the spectrum of the sample. The height and area of the near-edge band in a zinc spectrum were quantitatively proportional to the amount of zinc species.

3. Results and discussion

About 50 g of the phosphor wastes were filled uniformly in the cell (Fig. 1) and saturated with 0.01 M potassium nitrate as a conductive solution. X-ray pathway was fixed at the distance of 1.5 cm from anode. A 5 V/cm (direct current) was applied across Pt electrode pairs during the electrokinetic experiments.

Time dependence for the percent recovery of zinc from the phosphor waste under the electric field of 5 V/cm is shown in Fig. 2. After 90 min of electrokinetic treatments, about 42% of zinc was migrated to the cathode where zinc might be concentrated.
and recycled. Prolonging the electrokinetic treatment time to 4 h under the electric field of 5 V/cm, at least 80% of zinc in the phosphor waste can be recovered.

Speciation of zinc in the phosphor waste during electrokinetic treatments was also studied by in situ XANES spectroscopy (shown in Fig. 3). Generally, the intense absorption feature (white line) at 9667 eV in the Zn K-edge XANES spectra can be assigned to 1s to 4p transitions. In Fig. 3, mainly Zn(II) species (completely filled 3d shells of zinc) are found in the phosphor waste. The least-square fitted XANES spectra show that the main zinc species in the phosphor waste are ZnS (77%), Zn(OH)₂ (13%) and ZnO (10%). After the electrokinetic treatments for 60 min, Zn(OH)₂ was completely dissolved. 25% of ZnS and 4% of ZnO were also dissolved into the aqueous phase, and about 42% of zinc in the phosphor waste was enriched on the cathode after 90 min of the electrokinetic treatments (5 V/cm).

4. Conclusions

By in situ XANES spectroscopy, we found that during the electrokinetic treatments, ZnS (25%), Zn(OH)₂ (13%) and ZnO (4%) were dissolved as Zn²⁺. About 42% of zinc was enriched on the cathode under the electric field. Prolonging the electrokinetic treatment time to 4 h under the electric field of 5 V/cm, at least 80% of zinc in the phosphor waste was recovered. This work illustrates the usefulness of in situ XANES for revealing speciation of zinc in a solid waste during the electrokinetic treatments.

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References