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Remediation of rare earth elements (REE)-rich waters by precipitation of newly-formed phases.

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The "Ría de Huelva" estuary (SW Spain) is highly affected by acid mine drainage and phosphate fertilizer industry effluents, which contain high concentrations of dissolved metal(loid)s, some of them of high economic interest such as Rare Earth Elements (REE). These elements are essential for the energy transition as they are used in various applications necessary for the production, transport, and accumulation of electrical energy from renewable sources. However, high dissolved concentrations of REE could have a significant environmental impact on aquatic organisms [1]. This research work focuses on the remediation of REE-laden solutions with different concentrations of these metals, using a sorption strategy with mineral phases such as gypsum ($\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$) and brushite ($\text{CaHPO}_4 \cdot 2(\text{H}_2\text{O})$), where these elements of high economic interest may be concentrated for its potential recovery. The main objectives of this research were to determine: (1) the removal processes of dissolved REEs, as well as (2) the preferential incorporation in the minerals studied. For this purpose, precipitation experiments of REE-rich sulfate and phosphate phases were carried out in the laboratory. The liquid and solid samples resulting from the precipitation experiments were analyzed by atomic emission spectroscopy with inductively coupled plasma (ICP-AES), mass spectrometry with inductively coupled plasma (MS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission Fourier transform infrared (FTIR), which allowed us to determine the capacity for REE incorporation by the tested minerals, as well as possible changes in the characteristics of the newly-formed phases. The concentrations of REE in the sulfate and phosphate phases increased progressively as solutions with higher concentrations of these metals were used in the laboratory experiments. However, the removal percentages of REE by gypsum precipitation were noticeably lower than those by brushite precipitation. This could be because brushite has a greater adsorption capacity than gypsum, as both mineral phases have similar crystalline structures and therefore the co-precipitation processes of REE with both minerals should be similar. These results show that the removal of REE from solutions during the precipitation of newly-formed phases could be a viable strategy for the concentration of these valuable elements and the remediation of contaminated waters.

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[1] Oral, R., Bustamante, P., Warnau, M., D'Ambra, A., Guida, M., Pagano, G., 2010. Cytogenetic and developmental toxicity of cerium and lanthanum to sea urchin embryos. *Chemosphere* 81:194-198.