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Int J Waste Resour 2016, 6:3(Suppl)
http://dx.doi.org/10.4172/2252-5211.C1.003

2nd World Congress and Expo on

Recycling

July 25-27, 2016 Berlin, Germany

Innovative TiO_2-based recognition nano-devices for controlling the selectivity towards lanthanides ionic separation

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Rare earth (RE) elements are used in an ever-increasing variety of applications in new green and low-carbon technologies such as catalysis, permanent magnet, rechargeable NiMH batteries, lamp phosphors and biomedical applications among others. Their recovery needs contributions of chemistry and physical chemistry of selective extractive systems since the separation of the RE mixtures into individual elements is usually a complex and expensive process. (Mesoporous) silica-based nanocomposites prepared by sol-gel hydrolysis and containing amido, imido, polyamine, and CMPO ligands or self-assembled monolayers of lanthanide-selective ligand (SAMMS™) were studied for the recovery of RE. Non silicate systems are rare and require the need of a reliable and reproducible functionalization route as we previously reported. However, new hybrid metal oxide-based nanosorbents as a potential system to develop new separation techniques are of significant relevance. Herein, we present the results on the preparation and use of a series of novel modified DTPA-based ligands grafted onto TiO_2 nanoparticles in order to provide a better understanding of the requirements in hybrid nanomaterial design as selective ionic separation devices. We demonstrate that DTPA-functionalized nano-titania devices for efficient lanthanide ionic separation (La/Gd) with excellent selectivity (SGd/La around 150) can be reached through the right balance between the ligand affinity towards the metal (in relation to the nature and flexibility of the ligand) and the self-agglomeration (trough supramolecular interactions) of the nanocrystals. These results will be addressed in detail in order to provide useful guidelines for design of future nano-structured ionic recognition device in the separation of strategic metals for recycling economy.

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Solid sorbents for rare earths recovery from electronic waste

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Today there is an increasing need for Rare Earths (REs) due to their usage in numerous high-technology applications. Currently each EU citizen produces about 17 kg of Waste Electrical and Electronic Equipment (WEEE) per year. These wastes are rich in precious and strategic metals and, in many cases, are characterized by higher REs contents than those of natural minerals. Accordingly, recycling can be considered a valuable opportunity: This perspective is known as "urban mining". For these reasons, the study of a targeted and efficient REs recovery from WEEE can only lead to undeniable both socio-economic and environmental benefits. Activated carbon (AC) and modified AC were tested as solid sorbents at the purpose. The modified AC was synthesized by loading pentaethylenehexamine and the amount of loaded amine was estimated by COD analysis of the residual amount in solution. The AC and the modified AC were contacted with lanthanum solutions (chosen as representing element of REs family) and the lanthanum adsorbed by the solids was analyzed by ICP-OES of the contacted solution. Finally, release tests were performed on the different samples in order to verify the solids capability not only to capture but also to recover metal ions. The obtained results showed that the experimental procedure was appropriate to load the amine onto the AC and that the modification of the AC improved both adsorption (from 44% to 100%) and release (from 65% to 91%) with respect to natural AC, ensuring a global recovery efficiency of 90%.

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