Development of ion imprinted polymers for the selective extraction of lanthanides from environmental samples

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The analysis of the lanthanide ions present at trace level in complex environmental matrices requires often a purification and preconcentration step. The solid phase extraction (SPE) is the most used sample preparation technique. To improve the selectivity of this step, Ion Imprinted Polymers (IIPs) can be used as SPE solid supports. The aim of this work was the development of IIPs for the selective extraction of lanthanide ions from environmental samples. Two IIP synthesis approaches were evaluated. The first one, called trapping, is based on the use of non-vinylated ligands, which are trapped non-covalently in the polymer network. The second one involves ligands with vinyl moieties allowing their chemical immobilization by covalent bonds in the polymer matrix.

In a first part, IIPs were prepared according to the trapping approach using 5,7-dichloroquinoline-8-ol (DCQ) as non-vinylated ligand. For the first time, the loss of the trapped ligand during template ion removal and sedimentation steps was demonstrated by HPLC-UV. Moreover, this loss was not repeatable, which led to a lack of repeatability of the SPE profiles. For the first time, it was demonstrated that the trapping approach is not appropriate to synthesize IIPs for SPE use.

In a second part, IIPs were synthesized by chemical immobilization of methacrylic acid as functional monomer. The repeatability of the synthesis was confirmed by applying the same optimized SPE protocol on different IIPs resulting from different syntheses. A good selectivity of the IIPs for all the lanthanide ions was obtained. After optimizing the SPE protocol, IIPs were successfully used to selectively extract lanthanide ions from tap and river water.

Finally, IIPs were synthesized by chemical immobilization of methacrylic acid and 4-vinylpyridine as functional monomers and either a light (Nd³⁺) or a heavy (Er³⁺) lanthanide ion as template. Both kinds of IIPs led to a similar selectivity for all lanthanide ions. Nevertheless, this selectivity can be modified either for light or heavy lanthanide ions by changing the nature and the pH of the washing solution used in the SPE protocol.

Keywords: lanthanides, ion imprinted polymers, solid phase extraction, natural waters