Hg(II)-imprinted polymer gels – smart materials for mercury determination and speciation

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ABSTRACT

Ion imprinted polymers (IIPs) are a new generation synthetic "smart" materials with artificially generated recognition sites able to specifically rebind target chemical species [1, 2]. These materials are obtained by a cross-linking copolymerization of functional monomers around a template ion, leading to a highly cross-linked three-dimensional network polymer. The choice of the right functional monomer and chelating ligand is very important because this will determine, on one hand, the stability of the complex formed before and during the polymerization process and, on the other hand, the subsequent ability of the IIP to interact selectively with the target ion. The advantage of IIPs is that they can respond to external stimuli, as well as they show highly selective recognition ability toward template ion species.

In this study, Hg(II) imprinted copolymer gels (Hg(II)-IIPs) are prepared and used as smart sorbents for selective solid phase extraction of mercury ions from surface water samples. Hg(II)-IIPs are synthesized by dispersion copolymerization of 1-vinylimidazole, methacrylic acid or 2-hydroxyethyl methacrylate as functional monomer, trimethylolpropane trimethacrylate as cross-linking agent and 2,2'-azoisobutyronitrile as initiator in the presence of a Hg(II)–1-(2-thiazolylazo)-2-naphthol (Hg(II)-TAN) complex. The chemical composition, structure and morphology of the prepared Hg(II)-IIPs are defined using elemental microanalysis, Fourier transform infrared spectroscopy, scanning electron microscopy, and nitrogen adsorption–desorption measurements. The extraction efficiency (enrichment factor, selectivity, capacity) of the Hg(II)-IIPs toward inorganic mercury ion (Hg(II)) are studied using batch procedure. The optimal pH value for the quantitative sorption is 7, and full desorption is achieved by 0.1 M thiourea in 0.1 M HCl. The Hg(II)-IIPs exhibit excellent selectivity towards Hg(II) over methylHg, Cu(II), Cd(II), Fe(III) and Pb(II), due to the introduced memory effect. The prepared copolymer gel with 1-vinylimidazole as a functional monomer has higher capacity and selectivity towards Hg(II) than the copolymer gels prepared using methacrylic acid or 2-hydroxyethyl methacrylate. Adsorption process is characterized by Langmuir isotherm model. Analytical scheme for Hg speciation and enrichment in surface waters is developed based on the high selectivity of Hg(II)-IIPs toward Hg(II).

REFERENCES

[1] I. Karadjova, T, Yordanova, I. Dakova and P. Vasileva, "Smart Materials in Speciation Analysis", in *Handbook of Smart Materials in Analytical Chemistry*, 1st Edition, Vol. 2, John Wiley & Sons, 2019.

[2] Y. Ge, B. Butler, F. Mirza, S. Habib-Ullah and D. Fei, "Smart molecularly imprinted polymers", *Macromol. Rapid Commun*., vol. 34, pp. 903–915, (2013).

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