Synthesis of a novel polyurethane-based-magnetic imprinted polymeric nanoparticles for the selective optical detection of 1-naphthylamine in drinking water

Ángel Valero Navarro[a], **Francisco J. Orriach-Fernández[b],** Antonio L. Medina-Castillo[a], Jorge F. Fernández-Sánchez[b], Alberto Fernández-Gutiérrez[b]

[a]NanoMyP®, Nanomateriales y Polimeros S.L., Spin-Off company of the UGR, BIC building, Avd. Innovacion 1, 18100, Granada, Spain
[b]Department of Analytical Chemistry, University of Granada, Avda. Fuentenueva s/n, 18071 Granada, Spain Organization, Address, City, Country
avalero@nanomyp.com

Abstract

We present a magnetic optical sensor MIP which has been developed by synthesizing the first polyurethane based magnetic-molecularly imprinted polymer (mag-MIP) for the selective detection of (1-NA) in drinking water [1]. 1-naphthylamine (1-NA) is one of the top-priority contaminants and one of most important substructures of potentially carcinogenic pollutants discharged from pharmaceutical, dyestuff, photographic, agrochemical industries and cigarette smoke. Thus, its efficient detection in surface and ground waters has taken on increasing environmental concern.

The use of molecularly imprinted polymers (MIPs) has emerged as a promising tool to enhance the selectivity of luminescence sensing systems, owing to their specificity toward the target molecules and high stability. MIPs are made by synthesizing highly crosslinked polymers in the presence of “printing” molecules (templates). After removal of the template, the polymer can be used as a selective medium for the template molecule or structurally related compounds. MIPs combine highly selective molecular recognition properties which are comparable to those of biological system, with characteristics such as physical robustness, and good thermal, chemical and mechanical stability.

Most MIPs are typically synthesized by solution polymerization and there are many problems associated with this kind of methodology. Typically, when MIPs are prepared by solution polymerization, the resultant monolith has to be crashed, ground and sieved to produce microparticles for their applications. Particles obtained in this manner are irregular in shape and size and only 30-40 % is recovered as usable material. Precipitation polymerization (PP) is one of the most attractive and reliable methods available for the routine production of imprinted polymer microparticles with desirable characteristics. To our knowledge most of the MIPs that have been synthesized by this method of polymerization are acrylic or vinylic materials, so it is an unexplored challenge to make precipitation polymerization with other materials, such as polyurethanes.

The use of nanoparticled MIPs appears to be a very interesting alternative to obtain new powerful recognition materials that can be used in the development of optical sensors due to their inherent characteristics (robustness, good thermal, chemical and mechanical stability and their recognition properties). The application of MIPs for optical sensors, however, is not always successful [2]. The three main reasons for this are: **1)** if the analyte is not fluorescent, it is challenging to find a good transducer, **2)** the low sensitivity in many cases and **3)** the difficulty to implement the resulting MIPs in a fiber optic system without losing sensitivity and selectivity.

All these problems can be minimized by the incorporation of magnetic properties into the sensing material. It allows the in situ formation of sensor spots by magnetic separation and, consequently, optical readout from the outside or an easy way to fix a MIP at the tip of an optical fiber. With this aim we have synthesized the first polyurethane based magnetic-MIP for the selective detection of 1-NA in drinking water. The synthesis has been carried out in a two-step process: First, the encapsulation of magnetite-coated-oleic acid nanoparticles (γ-Fe_3O_4-OA) into a lipophilic polymeric matrix (poly-MMA-co-EDMA; 40 wt% MMA and 60 wt% EDMA) to obtain super-paramagnetic hybrid nanoparticles (SPHNs) by two steps miniemulsion-polymerisation; and second, the encapsulation of these magnetic seeds into the MIP structure by precipitation polymerization.

For the preparation of mag-MIP, the template naphthalene (0.20 mmol), bisphenol A (0.70 mmol), MDI (0.82 mmol) and phloroglucinol (0.33 mmol) were dissolved in a mixture of THF (8 mL) and SPHNs (16 mg; 4.5% w/w) in a 10 mL glass vial. The vial with the polymerisation mixture was sealed and let to polymerise with continuous mechanical stirring in the dark, at room temperature for 2 days. Non-imprinted polymer (mag-NIP) for use as control was also prepared and treated in exactly the same way, except that no template molecule was used during the polymerization stage.

The mag-MIP was first RHTEM imaged showing a well-organized material with magnetite within the material and the imprinted polymer coating the magnetic core (***Fig. 1***).

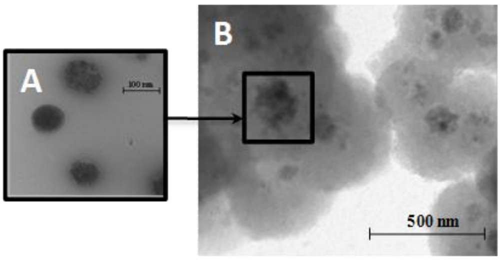

Fig. 1. HRTEM pictures of (A) SPHNs and (B) mag-MIP in which the SPHNs are located inside.

Thereafter, it was evaluated by batch rebinding analysis and the derived Freundlich isotherm, calculating the number of binding sites ($N_{K_{min}-K_{max}}$)= 2.63 and 0.79 mmol g^{-1}, for mag-MIP and mag-NIP, respectively) and apparent average adsorption constant ($K_{K_{min}-K_{max}}$)= 3.31 and 3.06 $mmol^{-1}$, for mag-MIP and mag-NIP, respectively) showing a very effective imprinting process.

We have also developed a magnetic optical sensor MIP by using an optical fiber coupled with a magnetic separator (***Fig. 2***).

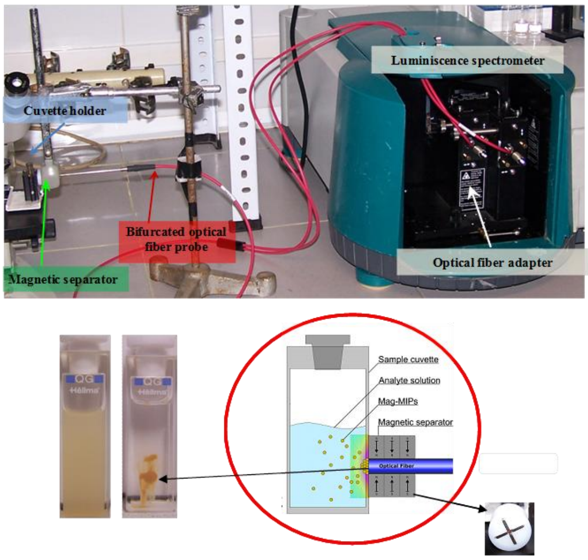

Fig. 2. Pictures of the measuring setup and the magnetic separator.

An unexpected selectivity for 1-NA was revealed allowing the detection of this molecule in water, even in the presence of 4 structurally related compounds (2-naphthylamine, 1-naphthol, 2-naphthol and 1-naphtalenemethylamine), with a low limit of detection (LOD) = 18 ng mL^{-1}. Finally, we applied this new hybrid material to the analysis of 1-NA in tap and mineral waters, obtaining a 91.6% average recovery rate.

References

[1] Angel Valero-Navarro, Antonio L. Medina-Castillo, Jorge F. Fernandez-Sanchez and Alberto Fernández-Gutiérrez, BIOSENSORS & BIOELECTRONICS, **11** (2011) 4520.
[2] Antonio L. Medina-Castillo, Günter Mistlberger, Jorge F. Fernandez-Sanchez, Antonio Segura-Carretero, Ingo Klimant and Alberto Fernandez-Gutierrez, MACROMOLECULES, **1** (2010) 55.