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Preparation of a Molecularly Imprinted Catalyst and its Application for Amperometric Sensor

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Abstract – Molecularly imprinted polymers (MIP) are artificial materials containing recognition sites with high affinity and selectivity. In the present study, a MIP was applied as a biomimetic catalyst for the specific recognition of 4-aminophenol (4-APh) to prepare amperometric sensor. The MIP was synthesized with 4-aminophenol (4-APh) as the template and two monomers, hemin to act as the catalytic center and methacrylic acid (MAA) used for building the active sites. MIP presented similar activity to the peroxidase. Under optimized conditions, the following analytical characteristics were observed: linear response range between 10.0 to 90.0 µmol L^{-1}, sensitivity from 5 nA L $µmol^{-1}$, limits of detection and quantification of 3.0 and 10.0 µmol L^{-1}, respectively. The morphology of the synthesized polymer was characterized by scanning electron microscopy analysis.

Considerable efforts have been made to create synthetic materials for mimicking biological recognition systems. Molecular imprinting has emerged as a simple and elegant method to impart recognition sites in synthetic polymers to interact with molecules of interest with specificity comparable to those of the biological entities like antibody and enzymes. In this sense, the introduction of molecularly imprinted polymers (MIPs) for sensor applications attracts increasing attention. MIPs are synthetic materials that possess tailor-made microcavities with molecular recognition capability for the target molecule. These materials mimic the recognition properties of the biomolecules by using the well known lock and key combinations. The present work describes, from an innovative and simple way mimicking peroxidase with MIP, the development of an amperometric sensor for 4-aminophenol (4-APh). Initially, the adopted synthesis was conducted strategically by the precipitation polymerization method with methacrylate acid, trimethylolpropane trimethacrylate, 2,2'-azobis-isobutyronitrile, and the insertion of Fe (III)protoporphyrin (IX) (hemin) in the synthetic route. Hemin was used as the prosthetic group responsible for mimic the peroxidase active site, creating, therefore, a catalytically active molecularly imprinted film for recognition of 4-APh. In order to evaluate the MIP and NIP performance (Figure 1A), polymers were synthesized in the absence and presence of hemin. The morphology of MIP film formed by the polymerization is shown in Figure 1B. It can be seen from the SEM micrographs that the precipitation polymerization gives a uniform, microspherical particles. Owing to control the separation point during precipitation polymerization that begins from a dilute monomer solution, uniform microspheres were obtained, which possessed higher surface areas and more complementary sites than those produced by bulk polymerization [1]. The amperometric sensor showed stability and best response for 4-APh recognition under an applied potential of - 0.1 V vs. Ag/AgCl in TRIS 0.05 mol L^{-1} (pH 7.0) buffer solutions containing a peroxide concentration of 100 µmol L^{-1}. Under such optimized conditions, the following analytical characteristics were observed: linear response range between 10.0 to 90.0 µmol L^{-1}, sensitivity from 5 nA L $µmol^{-1}$, limits of detection and quantification of 3.0 and 10.0 µmol L^{-1}, respectively (Figure 1C). The sensor showed high selectivity in presence of similar compounds and good stability for more than 80 successive determinations, with a repeatability of 2.7% (evaluated in terms of relative standard deviation) for n = 7. Furthermore, recoveries of 93–112% from water samples (tap water and river water) spiked with 4-APh were achieved, illustrating the accuracy of the proposed sensor.

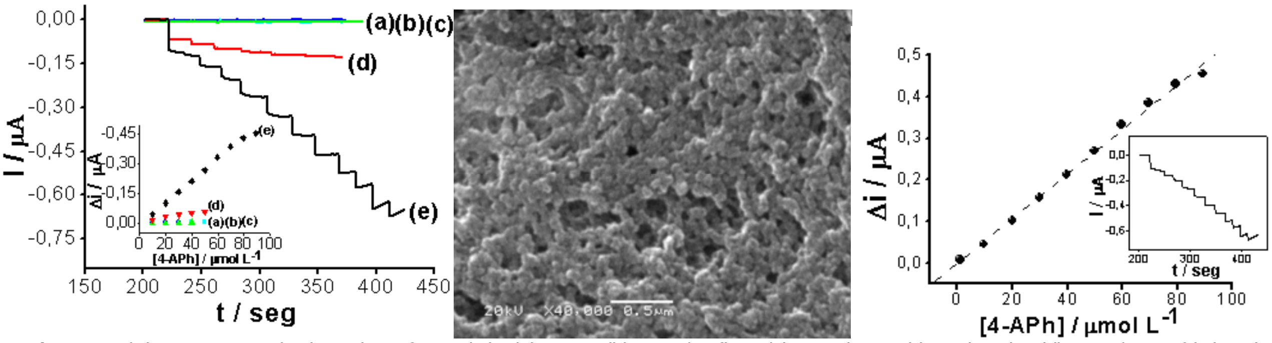

Figure 1: (A) Amperometric detection of 4-APh in (a) GCE, (b) GCE/Nafion, (c) GCE/NIP without hemin, (d) GCE/NIP with hemin and (e) GCE/MIP with hemin, **(B)** SEM image of MIP-4APh and **(C)** Calibration curve for 4-APh.

References

[1] M. Gallego-Gallegos et al. Journal of Environmental Management 90 (2009) S69.

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