Abstract of the doctoral thesis: 'Synthesis, characterization and application of polymeric materials based on silica matrices'

Author: M. Kujawska

Supervisor: Prof. dr hab. A. W. Trochimczuk

The dissertation presents the synthesis of molecularly imprinted polymers using two techniques based on silica materials: a hard template synthesis with functionalized structured silica as a matrix and Pickering emulsion polymerization in which the emulsion was stabilized by the presence of nanosilica. The process of polymers' synthesis, their characterization as well as the possibility of using obtained materials as selective adsorbents were thoroughly analyzed.

Synthesis with a structured silica template, containing the immobilized functional groups on the surface, made it possible to obtain a polymer with an ordered structure characterized by a narrow distribution of mesopores with the simultaneous development of a molecular imprint. In addition, the removal of the template, commonly causing a problem during the preparation of molecularly imprinted polymers, was simple and efficient, what is important from the point of view of sorption applications. Optimization of the synthesis showed that obtaining the polymer with the hierarchical structure of the pores constituting the interpenetrating network was possible with the use of MSU-F silica. In addition, the silica content in the polymerization mixture of 17 wt% was considered optimal because it allowed the preparation of structured material selective to the target substance. The subject of the research on a hard template synthesis were two groups of substances: β-blockers and neonicotinoids. In order to obtain polymers with selective active centers for the desired substances, the MSU-F silica was modified with 3-glycidoxypropyltrimethoxysilane and isopropylamine or 3-chloropropyltriethoxysilane and 2-chloro-4-aminopyridine, respectively. Sorption studies showed that prepared polymers contain active centers located on the surface of the material, what can be ascribed to the use of functionalized silica as a sacrificial template. This results in the availability of adsorption sites, and thus rapid adsorption of the adsorbate. Comparison with polymers prepared in the absence of a silica template showed that the use of functionalized silica during the synthesis caused about fourfold intensification of the sorption associated with the formation of the molecular imprint. Moreover, the binding sites are homogeneous, what was confirmed by a good fitting of experimental data using the Langmuir adsorption model. Furthermore, analyzed materials are capable of selective adsorption of the target molecules from a mixture of compounds with a

similar structure. However, greater selectivity was observed in the case of the material sensitive to the presence of β-blockers than neonicotinoids. In addition, it was showed that quick and quantitative desorption of the analyte from the surface of the polymers is possible, what allows the use the materials as specific adsorbents. The dissertation presents an exemplary use of materials as fillings of columns for solid-phase extraction and chromatographic column.

Using the second of the techniques, namely Pickering emulsion polymerization, allowed to obtain a molecularly imprinted polymer in the form of regular spheres selective for S-naproxen. A detailed optimization of the polymer preparation was carried out by performing a series of synthesis with varying functional monomer, crosslinking agent, the amount and type of porogen, as well as the content of the template in the polymerization mixture and the type of surfactant supporting stabilization of the emulsion. On the basis of sorption studies it was showed that in order to obtain a polymer with the desired properties 4-vinylpyridine in a tenfold excess to S-naproxen should be used as a functional monomer, ethylene glycol dimethacrylate as a crosslinking agent, toluene in a volume ratio 0.1 in reference to the monomer mixture and Tween 20 as the surfactant. The polymer prepared using optimized conditions is characterized by selectivity towards S-naproxen, which was confirmed by sorption studies from both single- and multicomponent solutions. The prepared material can be used for selective absorption of S-naproxen directly from aqueous solutions, however, the use of 5% ethanol in the sorption solution is advantageous because it minimizes the impact of non-specific binding. In addition, the disturbance of the interaction between the polymer and the analyte due to the use of the eluent being a mixture of the organic solvent and the alkaline solution causes a quantitative desorption of S-naproxen, which promotes the use of the material as a selective adsorbent in solid phase extraction.