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Salicylic acid and derivatives anchored on poly(styrene-*co*-divinylbenzene) resin and membrane via a diazo bridge: Synthesis, characterisation and application to metal extraction

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Abstract

New materials for chelating solid-phase extraction have been prepared by grafting of salicylic acid and derivatives on poly(styrene-*co*-divinylbenzene) based sorbents. These sorbents are either resin bead-shaped Amberlite® XAD-4 or membrane disk-shaped Empore™ SDB-XC. Grafting has been achieved via –N=N– spacer. The grafted ligands are salicylic acid (SA), its dimer form methylenedisalicylic acid (MDSA) and trimer form aurintricarboxylic form (ATA) in order to study the influence of multi-functionalization on chelating properties. Grafting scheme was validated on a model molecule (4-ethylaniline) for optimisation of experimental conditions. The resulting sorbents have been characterised by FTIR, Py-GC/MS analysis and ^{13}C CP-MAS NMR. Grafting rates are higher for SA (25–38%) than for MDSA (16–17%) and ATA (9%), still the number of SA entities remains almost constant. Metallic sorption abilities of the two new sorbents – determined by ICP-AES – have been succcessfully assessed by means of flow-through experiments with synthetic solution of multielement cations (Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+} and Al^{3+}). It evidenced the influence of the PTFE matrix, contained in Empore disks, for acidic pH. Finally, complexing capacities for Fe(III) were found to be higher for membranes (13.4 ± 0.7 for SA) than for resins (11.6 ± 0.6): this allows to consider grafted polymer membranes as competitive materials for SPE applications.

Keywords: Poly(styrene-*co*-divinylbenzene); Empore membrane; Amberlite XAD-4 resin; Salicylic acid; Methylenedisalicylic acid; Aurintricarboxylic acid; Solid-phase extraction

1. Introduction

Analysis of metal ions in aqueous samples commonly requires a preconcentration step to overcome

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the lack of sensitivity or selectivity of analytical methods [1]. This can be achieved by use of solid-phase extraction (SPE) which is based on the partitioning of the analyte between the solution and a solid sorbent [2]. SPE is now widely developed and has known a lot of significant advances in recent years [3]. According to the nature of the solid sorbent, retention mechanisms can be different: adsorption, ion exchange or chelation [4]. Chelating solid-phase extraction is a method particularly adapted for the analysis of trace metallic ions in polluted waters [5]: it requires the use of a sorbent modified by a ligand possessing high selectivity to the targeted metal ion.

Organic sorbents can be preferred to inorganic based sorbents like silica gel because of their selectivity and their stability over a wide range of pH [6]. Among them, resins composed of poly(styrene-*co*-divinylbenzene) (PS-DVB) [7,8] and especially commercial Amberlite® XAD-4 resin known as a macroporous PS-DVB resin are widely used to prepare chelating sorbents [9,10].

More recently, membranes containing PS-DVB beads embedded in PTFE have been developed by 3 M under the trademark Empore and used for recovery of organic compounds [11,12]. They present the advantage that fibrillated PTFE is inert to chemical modifications contrary to glass fiber matrix also used for membrane disk preparation. Some authors have used them for determination of metallic ions either by impregnation of colorimetric reagent on the surface of the membrane [13], by collection of a precipitate (metal-organic reagent) on the surface of the disk [14] or by binding of a surfactant complex to the support [15]. In the present paper, we propose an alternative route to the use of such SPE sorbents which consists in a chemical modification of PS-DVB by grafting of an organic ligand. This will allow to combine the advantages of chelating resins with those of membrane disks: less risk of plugging by suspended particle matter [16], limitation of the sorbent mass requisite for extraction and of the amount of solvent needed for elution [17], less variation between sample devices [18].

The ligands chosen for this study are salicylic acid (SA) and two of its derivatives: a dimer form, methylenedisalicylic acid (MDSA), and a trimer form, aurintricarboxylic acid (ATA) also commonly called aluminon (Fig. 1). For comparison, grafting of these compounds has been achieved both on free PS-DVB resin beads (Amberlite® XAD-4) and PS-DVB embedded in a PTFE fiber disk (Empore™ SDB-XC), in both case via a diazo bridge.

2. Experimental

2.1. Materials

Amberlite® XAD-4 resin was obtained from ACROS ORGANICS. Empore™ SDB-XC membrane disk (47 mm diameter) was produced by 3 M and purchased from VARIAN. Both sorbents were previously cleaned out in methanol during 24 h, rinsed with diethyl ether, and dried at 80 °C before use.

Salicylic acid (SA) and aurintricarboxylic acid (ATA) were purchased from SIGMA, methylene disalicylic acid (MSA) from ACROS ORGANICS. All other chemical reagents were purchased from ACROS ORGANICS and used as they were. Solutions of metals were prepared from dilution of 1 g L^{-1} atomic standard solutions (ALDRICH) in ultra high quality water (milli-Q Water System Millipore, St Quentin en Yvelines, France).

2.2. Instrumentation

A special glass reactor was designed for membrane modification. Three membrane disks can be fixed on a Teflon stage with nuts and the medium is mechanically stirred thanks to the central stem.

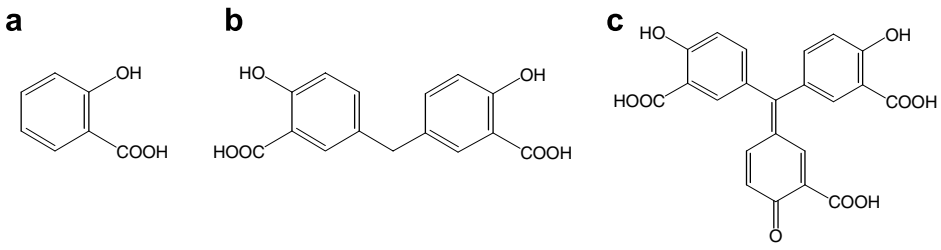

Fig. 1. (a) Salicylic acid (SA), (b) Methylenedisalicylic acid (MDSA) and (c) Aurintricarboxylic acid (ATA) molecules.