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Cationic imprinting of Pb(II) within composite networks based on bovine or fish chondroitin sulfate

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Abstract

Imprinting chondroitin sulfate (CS)/silica composites with Pb(II) and Cu(II) cations was explored with CS of bovine and different fish species origin. The process was based on the assumption that particular arrangements of the linear CS chains in aqueous solution, induced so as to accommodate cross complexation with the cations, would be embodied into a tridimensional matrix created through an organoalkoxysilane sol-gel scheme. The presence of Cu(II) in the synthesis of the composites did not result in the production of significantly stronger Cu(II)-oriented binding arrangements, and therefore, the imprinting was not successful. Inversely, for Pb(II), the materials obtained exhibited a "memory" effect for the Pb(II) ions, expressed in the observation of stronger (13%-44%) binding as compared to the nonimprinted counterparts, and increased selectivity (1.5-2 folds) against Cd(II). The imprinting features observed were dependent on the CS source. However, it was not possible to identify, among a set of their properties (carboxylate and sulfate abundance, percent of disulfated units, 4S/6S ratio, and molecular weight), any that correlated directly with the observed imprinting features. The augmented selectivity provided by the cation-imprinting process may be advantageous in areas such as analytical separation, remediation, purification, sensing, and others, particularly in those cases where a certain cation is of special interest within a mixture of them.

KEYWORDS

cation-imprinting, chondroitin sulfate, composite, lead (II), sol-gel

1 | INTRODUCTION

It was recently reported a cross-linking scheme for chondroitin sulfate (CS),[1] a water soluble heteropolysaccharide of repeating disaccharide units comprising an amino sugar (*N*-acetylgalactosamine [GalNAc]) and glucuronic acid linked by β-(1 → 3) glycosidic bonds, and presenting sulfate groups ($-O-SO_3^-$) (Figure 1, left).

The process relies on a sol-gel reaction that delivers a rigid microporous biopolymer-silica composite, which maintains the original ability of CS to complex metal cations via the carboxylate and sulfate groups.[2–4] The composite allows thus the exploitation of the negatively charged CS for metal cation-related applications requiring nonsoluble forms of the biopolymer, such as cation recovery from solution or sensor preparation. Chondroitin sulfate may be considered a low-cost piece of biomass, being obtained from wastes (mostly cartilage tissues) generated in slaughterhouse and fisheries.[5] Different sulfation patterns are found in CS originating from different species, what implicates also different cation-binding modes.[6]

It is well known that the addition of metal cations to aqueous solutions of CS induces major alterations in the rheological properties, such as a raise in viscosity.[2] These effects are explained by the cross complexation, which brings together 2 or more polymer chains to a single complexation point (the cation), resulting, in certain conditions, in the precipitation of a gel. The driving force of such cross complexation comes mainly from the carboxylate and sulfate ligand groups of 2 different CS chains sharing a single central cation coordination center.[2–4] This phenomenon may be also seen from the perspective of the metal cation acting as a perturbation that greatly changes the spatial configurations of the CS chains. The presence of the cation results in the rearrangement of chains towards maximal complexation energy and chain-chain interaction.

