



Metal cation sorption ability of immobilized and reticulated chondroitin sulfate or fucoidan through a sol-gel crosslinking scheme



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ABSTRACT

An immobilization scheme, via glycidyoxypropyl-trimethoxysilane sol-gel crosslinking, of chondroitin sulfate (CS) or fucoidan (Fd), inspired by the biological silicate bridge found in CS, is presented here. It revealed to constitute a simple and effective way of producing biopolymer-silicate composites without compromising the carboxylate- and sulfate- groups of the biopolymers, those which play a determinant role in the binding to metal cations. In the case of the Fd composite, the immobilization process resulted in the ~4-fold enhancement of the negatively charged sorption sites, probably due to unfolding effects induced by the synthesis conditions. Textural analysis of the composites showed a microporous, low surface area (6–12 m²/g), microstructure which did not prevent the observation of relevant sorption features for metal cations, especially for Pb(II) and Cd(II). Rate constants (1–14 g/mg min⁻¹) and affinity constants (79–370 L/mg) in the same order of magnitude of chitosan-based sorbents were determined, whereas capacities (2–24 mg/g) were smaller than the generality of those same sorbents. Globally, the sorption of metal cations by the Fd composite was superior to that by the CS composite. Furthermore, high stability of the sorbents and acceptable reproducibility of the synthesis was observed. Overall, the developed scheme of immobilization of CS and Fd appears capable of providing an effective way for integrating these biopolymers into metal cation-related applications such as biosorption, sensing or separation.

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1. Introduction

Chondroitin sulfate (CS) is a glycosaminoglycan (GAG), a heteropolysaccharide composed of repeating disaccharide units comprising an amino sugar (*N*-acetylgalactosamine, GalNAc) and glucuronic acid (GlcA) linked by β -(1 \rightarrow 3) glycosidic bonds. Each unit presents sulfation in different carbon positions or no sulfation at all (CS-0). The sulfate groups ($-\text{O}-\text{SO}_3^-$) may be placed in GalNAc, carbon 4 (CS-A), 6 (CS-C, more common), both 4 and 6 (CS-E), or in positions 6 of GalNAc and 2 of GlcA (CS-D) and 4 of GalNAc and 2 of GlcA (CS-B) (Fig. 1a). CS is extracted from wastes (mostly cartilage tissues) generated in slaughterhouse and fisheries [1], constituting then a low-cost piece of biomass. Fucoidans (Fd) are another class of sulfated polysaccharides, extracted from brown seaweed algae, generally consisting of a backbone of L -fucopyranose residues linked by α (1 \rightarrow 3) bonds, which may enclose side branches containing fucopyranoses or other

glycosyl units, e.g. glucuronic acid [2] (Fig. 1b). The exploitation of negatively-charged sulfated polysaccharides such as CS and Fd for metal cation-related applications is still insipient when compared with that of other polysaccharides such as chitosan, extensively studied for the recovery of heavy metals in waste waters [3] or for the construction of sensing devices for heavy metals [4]. The presence of the $-\text{O}-\text{SO}_3^-$ groups in the structure of CS and Fd provides these polysaccharides with permanent negatively-charged points even at pH values as low as 2. The cooperativity between sulfate and the other nearby functionalities attached to the backbone of the biopolymers ($-\text{COOH}/\text{COO}^-$, $-\text{OH}$ and $-\text{NHCOCH}_3$ in the case of CS; same or adjacent saccharide $-\text{OSO}_3^-$ groups and $-\text{OH}$ in the case of Fd) envisage strong binding modes towards cationic species with different selectivity than the one associated to the most commonly studied polysaccharides. In the case of CS, a series of in-depth studies reported in the early eighties [5–7] (see also [8] for a review of work conducted prior to 1980) demonstrated that the binding of divalent and trivalent metal cations involved mainly the carboxylate and sulfate groups. Later it was shown that the prevalent group for the *in vivo* interaction with calcium (II) could be sulfate, depending on a great extent of the source of CS utilized

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