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Alginate gels as heterogeneous supports for the non covalent immobilization of chiral organocatalysts

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PURPOSE OF THE ABSTRACT

The main aim of this work was the heterogenization of an organocatalyst by adsorption on alginates (natural polysaccharides) and the evaluation of the catalytic performance in a model asymmetric reaction.

The use of organic molecules as catalysts (organocatalysis) has recently attracted attention as a powerful tool for the synthesis of chiral molecules in the field of asymmetric catalysis [1]. However, one of the main disadvantages of this strategy is its low values of TON and TOF (turn-over number and turn-over frequency, respectively), making recovery and reuse of the catalyst essential from an economic and environmental point of view. As a solution, immobilization (or anchoring) of the catalyst to a solid support (typically a polystyrene resin) by covalent bonds has been proposed, allowing recovery of the catalyst through simple filtration [2]. However, under this strategy, the functionalization of the support requires multiple synthetic steps in order to generate the appropriate functional groups that allow the anchoring of the organic molecule of interest. An alternative approach for the preparation of these catalytic systems is the immobilization of the active phase to an insoluble support by means of non-covalent interactions, which translates into a simpler strategy, where the preparation protocol is simplified to the addition of an organocatalyst to the adequate support in the right conditions [3].

In terms of a suitable support, alginates are quite striking candidates due to their abundance and physical chemical properties. Alginates are anionic polysaccharides mainly located in the cell walls of brown macro-algae and some special bacteria including Azotobacter and Pseudomonas [4]. The possibility to exploit this polysaccharide as a solid support derives from its natural tendency in an aqueous media to form gel spheres under acidic conditions, or in presence of multivalent ions, such as Ca2+ or Cu2+ [5]. Likewise, the high abundance of functional groups in alginate polymeric structure (i.e. 5.6 mmol/g carboxylate groups) and the dispersed 3D arrangement of the polymeric chains are responsible to allow an easy entrapment of catalytic species and the interaction with the substrates involved in a specific reaction.

In this way, the use of non-covalent interactions for the immobilization of an organocatalyst was the central axis of the present work. Our approach was based on the interactions between the most basic groups of a model organocatalyst and the carboxylic groups of the alginates in order to prepare a truly heterogeneous and active catalytic system for an asymmetric reaction. In this sense, the first aim was to optimization of the adsorption protocol of a model organocatalyst: 9-amino (9-deoxy) epi-quinine (QA), which is a primary amine derived from quinine (a natural Cinchona alkaloid), using alginate-based materials as solid supports. In this part, different adsorption parameters and alginate supports were evaluated, e.g. type of solvent, effect of the water, use of alginic acid gels, M2+ alginate gels and heterocationic gels of the type M2+-H+.

The second part of this work was the evaluation of the catalytic performance of the new materials in terms of i) activity; ii) stereoselectivity and iii) heterogeneity in the asymmetric addition of aldehydes to nitroalkenes (Michael addition). The result show that was possible to get a very active and enantioselective heterogeneous organocatalyst with a high conversion (> 95%) and excellent enatioselectivity (ee> 98%). The results obtained in

the QA immobilization on alginates confirm the possibility to use a cheap and renewable bio-polymer as heterogeneous supports for a model organocatalyst, by means of a simple and efficient procedure opening the way to a number of future green perspectives in asymmetric catalysts.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

Polysaccharide | chiral organocatalyst | gels | biobased materials

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