Penicillium citrinum IMMOBILIZED ON CHITOSAN TO STEREOSELECTIVE REDUCTION OF KETONES

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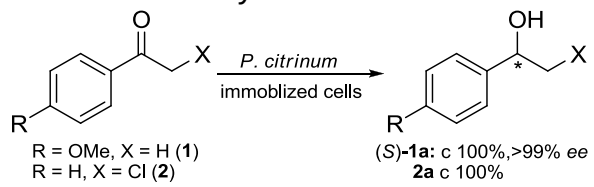
Chitosan, the *N*-deacetylated derivative of chitin, is a copolymer built of β-(1,4)-2-amino-2-deoxy-β-D-glucose and β-(1,4)-2-acetamido-2-deoxy-β-D-glucose units well-known to be biocompatible and biodegradable [1]. Biocatalytic processes can take advantage of the habitat-related properties of marine enzymes, such as salt tolerance, hyperthermostability, barophilicity and cold adaptivity [2]. The purpose of the present study was to evaluate the potential use of marine-derived fungus *Penicillium citrinum* immobilized on chitosan to the stereoselective reduction of *p*-methoxyacetophenone **1** and α-chloroacetophenone **2** (Scheme 1). *P. citrinum* was cultivated in liquid culture medium (1 L) under orbital shaker (130 rpm, 96 h, 30°C) [3]. Next, the mycelium was harvested by Buchner filtration. The mycelium (5.0 g) was poured into added to 250 mL) a 250 mL Erlenmeyer flask containing 5.0 g of chitosan and 100 mL of phosphate buffer (Na_2HPO_4/KH_2PO_4, pH 7, 0.1 M). The mixture was incubated at 32 ^oC for 24 h on an orbital shaker (130 rpm). Next, the immobilized cells were filtered and used in the biocatalytic reduction of ketones **1**-**2**. The control reactions were carried out using fungal mycelium not immobilized. The ketone **1** was reduced with moderate selectivity and conversion to (*R*)-alcohol **1a** (69% *ee*, c 40%) using the free cells of fungus. *P. citrinum* immobilized on chitosan catalyzed the quantitative reduction of ketone **1** to its corresponding (*S*)-alcohol **1a** with excellent selectivity and yield (>99% *ee*, yield = 95%). The whole cells (not immobilized) of *P. citrinum* catalyzed the reduction of ketone **2** to (*R*)-alcohol **2a** with low selectivity (31% *ee*, c 70%). *P. citrinum* immobilized on chitosan also catalyzed the reduction of ketone **2** to its alcohol **2a** with 100% conversion, but without selectivity.



Scheme. 1. Bioreduction of ketones **1**-**2** by *P. citrinum* immobilized on chitosan

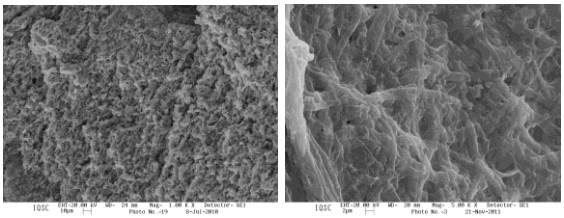


Figure 1. Scanning Electronic Microscopy. (**A**) Mycelia of fungus *P. citrinum*. (**B**) Mycelia of fungus *P. citrinum* immobilized on chitosan.

Scanning electronic microscopy (SEM) showed that the whole living cells of marine fungus *Penicillium citrinum* were efficiently immobilized on chitosan (Figure 1). These studies showed that immobilization of living cells of marine fungi for biocatalytic reduction of ketones depended on the type of xenobiotic substrates used.

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