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IN SITU EXTRACTION OF 3-HYDROXYPROPIONIC ACID ASSISTED BY MEMBRANE CONTACTOR

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In the actual environmental and economic context, there is an increased interest in the microbial production at a large industrial scale of the bifunctional weak carboxylic acids, the 2-hydroxypropionic acid (lactic acid) and its isomer the 3-hydroxypropionic acid (3-HP) (1). Among their various applications, these compounds are primarily sought for their direct use as building blocks mainly for the synthesis of bio-based polymers. Moreover, 3-HP has enormous potential for the production of commercially valuable chemicals. Although 3-HP is currently of limited usage due to its exclusive synthesis via chemical pathways (2), its market is expected to significantly grow up to a volume of 20,000 tons per year in 2015 according to a report of the International Energy Agency IEA-Bioenergy (2012) with a cost of 1,100 $ per ton (3). Moreover, in recent years, the tremendous growth of biodiesel manufacturing industries resulted in a large production of inexpensive and abundant available glycerol as by-product that could be used as substrate.

Until now, only lactic acid bacteria from the *Lactobacillus* genus have been shown to produce 3-HP from glycerol, although at low productivity (4). In the present work, the bioconversion of glycerol into 3-HP by *Lactobacillus reuteri* was studied. Product and its metabolic intermediate 3-hydroxypropionaldehyde (3-HPA) are suspected to exhibit inhibitory or toxic effects on the producing microorganisms, thus leading to low productivity and dilute product stream. This entails high costs for isolation and purification of the product. A potential strategy to relieve the inhibitory stress, to increase the performance of the microbial cells and to recover the molecule of interest is to implement an "*In Situ* Product Recovery" (ISPR), by which upstream bioconversion is combined to downstream extraction and recovery.

Although there are currently no ISPR technique developed in the literature for the extraction of 3-HP, some patents suggest that processes which proved to be effective for the extraction of its positional isomer 2-HP, could also be applied to 3-HP since both molecule exhibit quite similar physicochemical properties (5). A promising technique that drew a lot of attention lately for the extraction of 2-HP is the reactive extraction in an organic phase containing an extractant (6). In the present work, the extraction of 3-HP was studied using the long chain tertiary amine trioctylamine (TOA) or the quaternary ammonium salt tri-n-octylmethylammonium chloride (Aliquat 336) as extractants, and n-decanol as diluent. Comparison was made with 2-HP.

Results showed that the hydrophobicity and pKa differences between 3-HP and 2-HP had a significant impact on the performances of reactive extraction. Performing the extraction in a hollow fiber-membrane contactor provided a high interfacial area and allowed an important rise of the apparent distribution coefficient (K_{Dapp}). Extraction from a model binary solution of 3-HP in water was successfully performed in a membrane contactor. In addition, similar results in terms of extraction kinetic and yield were obtained when the medium was supplemented with the other molecules of the bioconversion pathway (Glycerol, 3-HPA and 1.3 propanediol), that confirmed the selectivity of the studied extraction process. These results thus demonstrate the high potential of this ISPR technique applied for the biotechnological production of 3-HP.

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