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Integration of electrodialysis into an enzymatic synthesis for the separation of phosphate from glucose-1-phosphate

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ABSTRACT

In biotechnological or other applications, electrodialysis can be an efficient method for the separation of phosphate from products with relatively high molecular masses (greater than around 200 kg/kmol), even though they are electrically charged. In this work, the separation of phosphate at high initial concentration (360 mM) from glucose-1-phosphate (G-1-P, 46 mM) was investigated. Around 90% of the phosphate could be removed, while 25% of G-1-P was separated. In this case, there is no product loss because phosphate could be recycled back to the reactor. Also at low concentrations ($C_P \sim 22$ mM), 77% of phosphate and only 20% of G-1-P, ($C_{G\text{-}1\text{-}P} \sim 30$ mM) were removed. The efficiency can be substantially improved with a two-step electrodialysis. The molar phosphate fluxes were considerably higher than the G-1-P (from around 4 to 40 times) at phosphate to G-1-P concentration ratios from 0.7 to 7. A theoretical consideration shows that this can be first of all attributed to a rather low mobility of G-1-P in the membrane matrix. The mobility of such substances in ion-exchange membranes depends also significantly on concentration.

1. Introduction

The development of separation processes for the recycling and recovery of substances, preferably closed-loop processes in production systems, is in general recommended. If a shortage/depletion of a substance is in discussion, like in the case of phosphate [1–3], the application of such technologies is of particular importance. There are various sources from which the separation and recovery of phosphate are of interest. These are for example wastewater and process streams [1,2,4], buffers from enzymatic reaction system or fermentation broth [5], liquid streams coming from biorefineries [6,7] and even urine [8]. As reported in many publications, there are some methods for the recovery of phosphate such as precipitation [4,9], adsorption [2,10] including membrane separation [1,5,11]. In case of membrane technique, the electrodialysis represents a useful method for this purpose. In the present work, this method was investigated in context to a biochemical reactions system, namely the enzymatic production of glucose-1-phosphate (G-1-P).

G-1-P is one of the physiologically important intermediates in carbohydrate metabolism. From the commercial point of view, several applications can be identified. For example, it can be used for medical purposes as an antibiotic, or as an immunosuppressive drug [12,13]. G-1-P can be prepared chemically through the phosphorylation of glucose-penta-acetate with phosphoric acid in a water free medium. An enzymatic synthesis using phosphorylases and starch or other carbohydrates including inorganic phosphate as substrate represents an alternative method. Regardless of the production process, the reaction mixture contains a certain amount of unreacted inorganic phosphate. The integration of an electrodialysis into the production offers the recovery and reuse of phosphate in a sustainable way (see Fig. 1).

The investigation focused mainly on the electrodialytic key process data: molar flux, energy consumption, relation between phosphate and G-1-P molar flux (selectivity) and process efficiency. Furthermore the influence of electrical potential (electrical current density) and concentrations on selectivity was examined. Both substances are in charged form however, the molecular masses, chemical structures and partially the valencies are different. Therefore, the results give some information about the electrodialysis when substances with electrical charges should be separated from each other. However, due to the relatively high molecular mass of G-1-P (M = 260 g/mol), the separation of phosphate is preferable. Two different cases were considered: (a) significant higher phosphate molar concentrations than G-1-P and (b) equal starting

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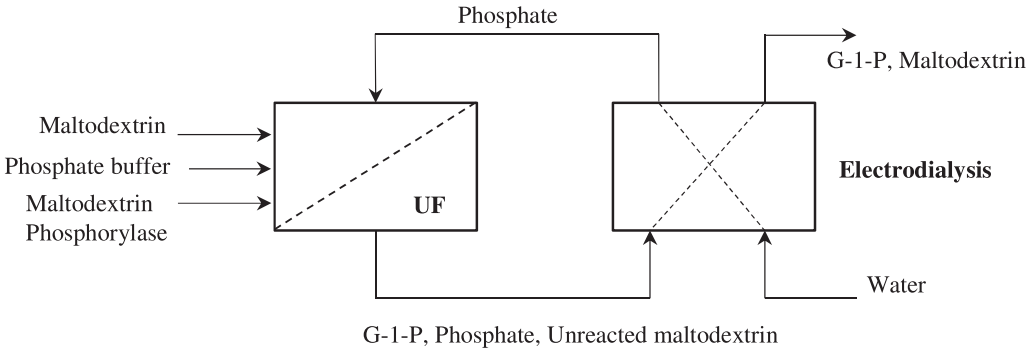

Fig. 1. Continuous production of G-1-P including downstream processing using electrodialysis.

concentration. A theoretical discussion was also included. The results may also be helpful when considering similar phosphate separation problems.

2. Materials and methods

An electrodialysis stack, suitable for membranes with an effective area of 37.0 cm^2, was equipped with 7 cell pairs. The thickness of the spacer, which determines the distance between the membranes, was 0.5 mm. AMX and CMX (anionic and cationic exchange membranes) were used (Table 1), which are available from Tokuyama Corporation, Japan. At the first and last membranes, two platinum wires were placed to measure the electrical potential only across the membranes excluding the electrodes. A 0.5 N Na_2SO_4 solution was used to rinse the electrodes. The flow rates in diluate and concentrate cells were 10 cm/s. The temperature was held at 303 ± 2 K. All trials were carried out in a batch recycle mode.

The composition of the G-1-P/phosphate solution was as followed: 360 mM potassium phosphate, 46 mM G-1-P and 20 mM unconverted substrate (maltodextrin). The pH-value was 7.3 and the conductivity was 4.0 S/m. The concentrations of G-1-P, phosphate, and maltodextrin were measured photometrically. In the case of G-1-P, the reaction of phosphoglucomutase in the presence of NAD and glucose-6-phosphate dehydrogenase was used [14]. For the phosphate, a test kit, Spectroquant 14842 from Merck was used. The concentration of maltodextrin was determined by the dinitrosalicylic acid (DNS) method. All experimentally values obtained in this study have an accuracy of ±10%.

2.1. Calculations

The molar flux (J_i) was calculated by Eq. (1):

$$J_i = \frac{V_{D,0}C_{i,0} - V_{D,t}C_{i,t}}{A_{eff} \cdot t} \quad (1)$$

where C_i is the concentration of specie i (mol/L), V is the volume of diluate, A_{eff} is the effective membrane area (m^2), and t is the time (s). Subscripts 0 and t refer to initial time and time t, respectively;

The specific energy consumption (E) can be calculated by the following equation

$$E = \frac{U_{cells} \int_0^t I(t)dt}{n_i} \quad (2)$$

where U_{cells} is the electrical voltage across all cells (excluding electrode) (V), I(t) is the electrical current (A) and n_i is the number of transported moles of specie i between time 0 and t.

The current efficiency (η) is defined as

$$\eta = \frac{\sum z_i n_i}{N \cdot \frac{1}{F} \int_0^t I(t)dt} \quad (3)$$

where z_i is the charge of an ion, N is the number of cell pairs and F is the Faraday constant (96,490 A s/meq).

Table 1
Properties of CMX and AMX membranes.

Property	CMX	AMX
Water content (%)	0.25–0.30	0.25–0.30
Electric resistance (Ω cm^2)	1.8–3.8	2.0–3.5
Ion exchange capacity (meq/g)	1.5–1.8	1.4–1.7
Transport number (Total cation or anion)	0.98	0.98
Thickness (mm)	0.14–0.20	0.12–0.18

3. Results and discussion

Firstly, it is helpful and necessary to know the ionization fraction of the individual compounds at different pH. As can be seen in Fig. 2, at the original operating pH value (7.3) the portions of mono and divalent phosphate were 60 and 40%, respectively. In case of G-1-P, the portions were 10% monovalent and 90% divalent. Fig. 2 shows also the chemical structure of G-1-P.

The following results represent two different situations: the starting molar concentration of phosphate is significantly higher than that of G-1-P (approximately 8 times higher) and the starting concentrations of both compounds are almost equal.

3.1. Case A: Separation of phosphate at concentrations significant higher than G-1-P

Before substances are separated by electrodialysis, it is advantageous or necessary to know at which maximum electrical voltage/-electrical current the process should be operated. This so called limiting current density can be determined for example by plotting the Ohm resistance against the reciprocal value of electrical current. Sometimes it is not easy to obtain a precise result, however as shown in Fig. 3 the resistance started to increase at reciprocal current density of 0.0068 m^2/A, which is equivalent to the limiting current density of 147 A/m^2.

For the subsequent separation of phosphate, the initial current density was adjusted to 117 A/m^2 which is 80% of the limiting current density. The corresponding electrical voltage (0.64 V per unit cell) was kept constant during the separation process. A 150 mM potassium phosphate solution was used in the concentrate circuit and the pH-value was adjusted to 7.0. The reductions in the concentrations of phosphate and G-1-P over time are shown in Fig. 4.

The experiment was stopped when the phosphate and G-1-P concentrations were almost equal at around 35 mM. As expected, the transport of phosphate was much higher than that of G-1-P mainly due to the significant higher concentration, lower molecular mass and partially due to the chemical structure. The pH value