Journal of Membrane Science 341 (2009) 46–50

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Cationic balance and current efficiency of a three-compartment bipolar membrane electrodialysis system during the preparation of chitosan oligomers

Fabrice Lin Teng Shee, Laurent Bazinet*

Institute of Nutraceuticals and Functional Foods (INAF), Department of Food Sciences and Nutrition, Laval University, Québec, Canada G1K 7P4

ARTICLE INFO

Article history:
Received 1 April 2009
Received in revised form 18 May 2009
Accepted 20 May 2009
Available online 27 May 2009

Keywords:
Chitosan oligomers
Bipolar membrane
Electrodialysis
Cationic balance
Current efficiency

ABSTRACT

Chitosan oligomers, known for their specific biological properties, were produced by an alternate method using a three-compartment bipolar membrane electrodialysis (BMED) system. The three main products (i.e. an acidified chitosan solution, a basified chitosanase solution and a demineralized chito-oligomer solution) were analyzed by inductively coupled plasma (ICP) for their cationic content as a function of BMED duration. It was found that sodium and potassium were the main cations present in the solutions. Using a current density of 10 mA/cm^2 for BMED, these cations were removed from the diluate compartment with constant migration rates of 0.30 and 0.37 mequiv. L^{-1} min^{-1}, respectively for sodium and potassium. The cationic balance showed that all cations were preserved during the electrodialysis treatment, and that 80% of the cations were distributed between the basified and the diluate compartments. In addition, a current efficiency of 80%, constant during all the process, was calculated from the total cations migrated in the basified compartment, confirming the energetical performance of the system.

1. Introduction

Chitosan oligomers are low-molecular-weight oligosaccharides produced from the hydrolysis of chitosan, a linear copolymer of β-1,4-linked 2-amino-2-deoxy-D-glucopyranose (GlcN) and 2-acetamido-2-deoxy-glucopyranose (GlcNAc) units [1]. The interests of chitosan oligomers are mainly due to their improved solubility and low viscosity in comparison with chitosan [2]. Moreover, chito-oligomers exhibit specific biological properties such as antifungal activity [3], antibacterial activity [4], antiviral activity [5], antitumor activity [6], and antioxidant activity [7]. Traditionally, the preparation of chitosan oligomers by enzymatic hydrolysis includes several steps consisting in chitosan solubilization by chemical acidification, incubation with chitosanase enzyme, and termination of enzymatic reaction by heating [8]. However, the resulting product usually presents a higher salt content due to the addition of external acid such as hydrochloric or acetic acid [9].

Recently, an integrated process for the preparation of chitosan oligomers using a three-compartment bipolar membrane electrodialysis (BMED) system was proposed as an alternative method to the conventional chemical preparation of oligomers [10]. The elementary cell consisted in an acidified compartment for chitosan solubilization, a basified compartment for enzyme inactivation after incubation and a diluate compartment for chito-oligomers demineralization (Fig. 1). This unique process ensued from results of studies on chitosan fouling during bipolar membrane electroacidification [11,12] and chitosanase inhibition by electrobasification [13]. The advantages of this system are the possibility to perform three steps in a single operation unit, the acid and base necessary for the process being generated *in situ* by the BMED system, and the low ash content of the chito-oligomer end product, due to the demineralization by homopolar ion-exchange membranes [10]. Furthermore, due to optimization of the BMED configuration, no fouling appeared during the process and it was demonstrated to be energy efficient [12,13]. However, no information is available in the literature about the ionic balance during such a three-compartment BMED process. The ionic equilibrium is important during an electrodialytic process since an important impoverishment of one compartment in ion (low ash content of the chito-oligomer end product) would increase the global system resistance and consequently will affect the current efficiency and the energy consumption [14–16]. Hence, Bazinet et al. [15] observed, for a two-compartment BMED process during electroacidification of milk, a decrease in electrical efficiency by a loss of electrogenerated H^+ through the cationic membrane, due to a lack of sufficiently mobile potassium ions, while Balster et al. [16] observed, for a three-compartment BMED process during electroacidification of milk, that the current efficiency of their process suffered from proton leakage at the anion-exchange membrane. Furthermore, the current efficiency is one of the most important

* Corresponding author. Tel.: +1 418 656 2131x7445; fax: +1 418 656 3353.
E-mail address: Laurent.Bazinet@fsaa.ulaval.ca (L. Bazinet).

0376-7388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2009.05.028

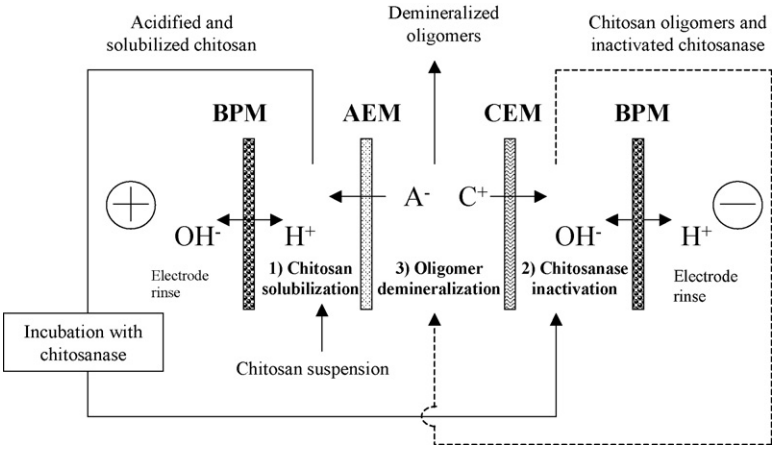

Fig. 1. Configuration of the elementary cell for the preparation of chitosan oligomers using a three-compartment bipolar membrane electrodialysis system. BPM, bipolar membrane; AEM, anion-exchange membrane; CEM, cation-exchange membrane; A^-, anions; C^+, cations.

process parameter proportional to the power consumption of a plant [17]. The current efficiency is calculated from the mass equivalent transported (E_m, in mol) by application of a direct electric current and based on Faraday's law [18–20]:

$$\sum E_m = \sum C_i V z_i = \frac{NtI\eta}{F} \quad (1)$$

where C_i is the concentration of the species i, V is the volume of the solution, z_i is the valence of the species i, N is the number of cell pairs, t is the duration, I is the current intensity, η the current efficiency of the system and F is the Faraday constant.

The number of mass equivalent migrated through the ion-exchange membrane is quantified experimentally and can be then compared to the theoretical one to determine the efficiency of the process [20]. This approach can only be used when the number of ionic species and their concentrations all along the process are well known, but allows to study the *in situ* evolution of the current efficiency during the process.

In this context, the main objective of the present study will be to characterize the ionic evolution in the three compartments through the cationic content of the treated solutions. The measurements of cationic content will be carried-out by inductively coupled plasma (ICP) on samples collected in the compartments at various electrodialysis time. Moreover, this work will be completed by an evaluation of the current efficiency based on the comparison between hydroxyl ions production and total equivalent cations migrated in the basified compartment.

2. Materials and methods

2.1. Chemical products

Chitosan and chitosanase enzyme were used as starting materials and were kindly provided by DNP Canada (Granby, QC, Canada). Chitosan presented a 96% deacetylation degree and an ash content of $0.40 \pm 0.01\%$ (w/w on dry basis). Chitosanase, isolated and purified from *Streptomyces* sp. N174, was kept at 4 °C until it was used for incubation with chitosan. Other chemicals included NaCl and KCl, both of reagent grades (Biorad, Québec, QC, Canada).

2.2. Electrodialysis equipment

The module was a MP type cell (100 cm^2 of effective surface) equipped with a Dimensionally Stable Anode (DSA®), and a 316 SS cathode from ElectroCell AB (Täby, Sweden). The ionic membranes, Neosepta BP-1 bipolar membranes, AMX-SB anionic membranes and CMX-SB cationic membranes were manufactured by Tokuyama Soda Ltd. (Tokyo, Japan) and purchased from Ameridia (Somerset, NJ, USA). The cell was connected to external reservoirs with a capacity of 10 L and the solutions were circulated using centrifugal pumps and flowmeters, using the same conditions as Lin Teng Shee et al. [10].

The elementary cell consisted in a three-compartment configuration (Fig. 1). The stack contained one pair of the elementary cell. The solutions were acidified, basified and demineralized in compartments 1, 2 and 3, respectively. Compartment 1 received the chitosan material to be solubilized by acidification in a 0.05 M NaCl solution (1.5 L) to reach 4.6 g/L of soluble chitosan at the end of treatment. The resulting chitosan solution was incubated in a separated reservoir during 12 h at 25 °C using chitosanase enzyme to produce chitosan oligomers. After incubation, the depolymerized chitosan solution was directed to compartment 2, where the chitosanase enzyme was inactivated by basification. Finally, the chitosan oligomer solution containing the inactivated chitosanase was circulated in compartment 3 for further demineralization of the oligomers. Before the three operation units could be carried-out simultaneously, some solutions (i.e. acidified chitosan and basified oligomer solutions) were prepared in preliminary experiments to initiate the process cycle; in this case, compartments 2 and 3 were filled with 2 g/L KCl solutions [10]. An additional fourth reservoir, filled with a 20 g/L NaCl solution was used as electrode rinse solution. The flowrate for all solutions was maintained at 4 L/min.

The electrodialysis treatment consisted in applying a constant current density of 10 mA/cm^2 during 60 min. The experiment was carried-out in triplicate. Samples of solutions (15 mL) were collected every 10 min from 0 to 60 min in the three main compartments for mineral analysis by inductively coupled plasma (ICP) and further calculations.

2.3. ICP analysis

The concentration of the cations (potassium, magnesium, sodium and calcium) in the collected samples was measured by inductively coupled plasma (ICP, Optima 4300 DV, PerkinElmer, Norwalk, CT) in radial view. The wavelengths used to determine potassium, magnesium, sodium and calcium concentrations were 766.49, 285.21, 589.59, and 317.93 nm, respectively [21].

2.4. Determination of current efficiency

The equivalent amount of cations migrated in the basified compartment was used to calculate the current efficiency of the system,