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Effect of solution flow velocity and electric field strength on chitosan oligomer electromigration kinetics and their separation in an electrodialysis with ultrafiltration membrane (EDUF) system

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ABSTRACT

The aim of the present work was to study the effect of solution flow velocity and electric field strength applied to an electrodialysis with ultrafiltration membrane (EDUF) cell on chitosan oligomer electromigration kinetics and on chitosan oligomer mixture fractionation. It was shown that the effect of solution flow velocity was not significant, while the electric field strength showed a significant effect on each chitosan oligomer electromigration rate. The effect of the electric field strength was also significant on the separation possibility of the studied oligomers. It was shown that by using electric field strength of 2.5 V/cm, it was possible to obtain a solution composed only of the dimer and trimer until an operating time of 2 h. By increasing the electric field up to 5 and 10 V/cm, it was no more possible to separate the chitosan oligomers. Chitosan oligomer transport numbers were measured. It was found that they contribute to about 7% of total electric current carrying, while about 93% of the total electric current could be carried by the electrolytes. The system performance was also evaluated through electric field intensity measurement and membrane integrity evaluation. It was found that the membranes kept their integrity and no significant fouling was detected. EDUF appeared consequently as a very interesting and innovative technology for the separation at a large scale of oligosaccharide.

1. Introduction

Electrokinetic separation process is one of the most promising in situ technologies for the removal, separation and purification of bioactive charged molecules from complex solution made of charged and non-charged components [1–3]. A separation by an electrokinetic phenomenon takes place when an external electric field is applied to a system in which a porous barrier was introduced [4]. In such system, electrophoresis becomes the principal electrokinetic phenomenon for charged molecules migration [5]. Based on physicochemical and electrokinetic properties of solutes in the feed solution, some of these molecules could be removed from the feed solution in order to obtain pure or enriched fractions [6].

The electrokinetic processes were successfully applied to a variety of molecules. It was reported that organic molecules such as benzene, toluene, ethylene, xylene and trichloroethylene, could be moved using electrokinetic processes [7,8]. The electro-transport and removal of polar organic molecules such as phenols, acetic acid, butyric, valeric, adipic, caproic and oxalic acids have been also investigated [9–11]. In food and biotechnology fields, several authors successfully used hybrid electrokinetic processes for separation and purification of bioactive molecules. Hence, it was reported that an electrophoretic membrane contactor was used for electroseparation of binary mixtures made of poly(L-glutamic) acid, α-lactalbumin and bovine haemoglobin [12]. They showed that solute flux through the ultrafiltration membrane used increased by increasing the product of electric field strength and the residence time. In this study, the solution flow velocities used were fixed at 1.66 and 83.33 mL/min, respectively. In other studies by Poulin et al. [13–15], cellulose ester ultrafiltration membranes were stacked in an electrodialysis cell for simultaneous separation of bioactive peptides produced by an enzymatic hydrolysis of β-lactoglobulin. It was shown that with one ultrafiltration membrane, increasing the overall applied voltage by a factor 2 and 4 resulted in increasing of the final peptide concentration by the same factor. Concerning the solution flow velocity (rate) effect, the following values were used: 100, 150, 200 and 250 mL/min [13]. The author showed that the solution flow velocity had no effect on the total peptide migra-

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tion in the permeate solution. However, at the highest value tested, the selectivity of the process was influenced and the migration of some peptides was lower at 250 mL/min.

Chitosan oligomers are bioactive molecules. They are widely used for different purposes in biotechnology and medicine [16]. It was demonstrated amongst others that chitosan oligomer tetramer has a significant effect to inhibit the adhesion of three strains of enterophathogenic *Escherichia coli* up to 30% of the level of adhesion seen in the controls (samples without chitosan oligomer) [17]. Some electrokinetic behaviors of chitosan oligomers (electrophoretic mobility) under different conditions have been studied [18]. Because of their cationic behavior in an acidic medium [18,19], electrodialysis with ultrafiltration membrane (EDUF) procedure was successfully used for chitosan oligomer mixture separation [20,21]. However, these previous studies concerned the effect of the molecular weight cut-off (500, 1000, 5000, 10,000 and 20,000 Da) of the UF membrane stacked in the ED cell [20] and the effect of the pH and cell configuration on the oligomer mixture separation performances [21]. Furthermore, both studies were carried-out at one fixed applied voltage (5 V or 2.5 V/cm) and flow velocity (300 mL/min.).

In a context of EDUF optimization for separation of chitosan oligomers, the aim of the present work was to study the effect of feed solution flow velocity and applied voltage to the electrodialysis with ultrafiltration membrane (EDUF) cell on the electromigration kinetics of the chitosan oligomers and impact on their separation possibility in order to produce pure or enriched fractions. Indeed, for the industrial use of EDUF, the major parameters allowing the more precise separation of the different oligomer is needed. Since the parameters tested in the present study have never been studied previously on chitosan oligomer separation, they could be of interest.

2. Materials and methods

2.1. Chemicals and materials

2.1.1. Chitosan oligomers

A mixture of three chitosan oligomers (dimer, trimer and tetramer), lot No W-040720 was gracefully provided by ISM Biopolymer (Granby, Québec, Canada). Standards of chitosan oligomers (dimer, trimer and tetramer) were purchased from Seikagaku Corporation (Japan, Cat. No: 800105) and purity not less than 98%.

2.1.2. Chemicals

All chemicals were of analytical grade. KCl and NaCl were purchased from Laboratoire MAT (Montreal, QC, Canada) and HCl was from Fischer Scientific (Nepean, ON, Canada). Acetonitrile of HPLC grade was purchased from EMD Chemicals Inc. (Gibbstown, NJ, USA).

2.1.3. Membranes

Ultrafiltration membrane with molecular weight cut-off (MWCO) of 10,000 Da from Spectrum Laboratories Inc. (Rancho Dominguez, CA, USA) and anionic exchange membranes AMX-SB (Tokuyama Soda Ltd., Japan) were used. The main characteristics (thickness, electrical conductivity) of these membranes are presented in Table 1.

2.2. Experimental

2.2.1. Electrodialysis with ultrafiltration membrane (EDUF) configuration

A MicroFlow type electrodialysis cell (ElectroCell AB, Täby, Sweden) with an effective area of 10 cm^2 was used. The EDUF cell configuration [Anode-AEM1-MUF-AEM2-Cathode] defines three closed compartments and was the same as the one described by Aider et al. [20]. The first compartment was for NaCl (20 g/L) as electrode rinse solution. The second one was for the chitosan oligomers solution and the third one for KCl (2 g/L) solution. Each compartment was connected to a separate external reservoir to allow recirculation of the solution. For all experiments, the anode/cathode voltage difference was supplied by a variable 0–60 V power source (HPD 30-10SX, Xantrex, Burnaby, BC, Canada). Once the EDUF cell was assembled, electrodes spacing was 2.0 ± 0.1 cm.

2.2.2. Protocol

Electroseparation by electrodialysis with ultrafiltration membrane (EDUF) treatments were carried-out on 200 mL of chitosan oligomer solution in a batch process at three applied voltages (5, 10 and 20 V) which corresponded to three average electric field strengths of 2.5, 5 and 10 V/cm. Solutions flow velocities of 2.77, 8.33 and 13.88 cm/s which corresponded to 100, 300 and 500 mL/min, respectively, were used. The chitosan oligomer mixture solution was obtained by dissolving chitosan oligomer mixture in HPLC grade water to obtain a final concentration of 3% (w/v). Its initial pH was adjusted to pH 4 by adding 1 N HCl. This pH value was selected following previous work on the effect of the pH value on chitosan oligomer electrophoretic mobility [19]. The pH of the 200 mL KCl solution in the adjacent compartment was also adjusted and was the same one as in the chitosan oligomer solution compartment. Samples of chitosan oligomer and KCl solutions were drawn at the beginning of the process before applying the external electric field and every 60 min during the treatment. EDUF was stopped after 4 h of treatment. During treatment, pH and conductivity values were recorded in the KCl and chitosan oligomer solutions. Measurements of the current intensity were used for the calculation of the total system resistance. Thickness and electrical conductivity of the membranes were measured before and after each treatment to check for their integrity and verify their potential fouling. All samples were analysed by HPLC to determine the electromigration rate of the three chitosan oligomers.

2.2.3. Analyses

2.2.3.1. Chitosan oligomer profiles. Chitosan oligomers in the treated solution and in KCl (migration compartment) were analysed using a Shodex Asahipak NH2P-50 column connected to a guard column NH2P50G 4A (Shodex Separation and HPLC Group, Kanagawa, Japan). The apparatus used was a Waters 715 equipped with an RI (refractive index) differential refractometer (Model 410, Waters Corporation, Milford, MA, USA). The eluent was CH_3CN/H_2O

Table 1
Electrical conductivity (κ) and thickness (l) of the 10,000 Da MWCO ultrafiltration (UFM) and anion exchange (AEM) membranes before and after electrodialysis with ultrafiltration membrane (EDUF) treatment.

Parameter	10,000 Da MWCO UFM		Anion exchange membranes (AEM) AMX-SB			
	Before	After	AEM-1		AEM-2	
			Before	After	Before	After
κ (mS/cm)	0.5207 ± 0.0039	0.5248 ± 0.0138	4.545 ± 0.118	4.542 ± 0.119	4.484 ± 0.127	4.479 ± 0.125
l (mm)	0.283 ± 0.002	0.283 ± 0.001	0.132 ± 0.001	0.131 ± 0.001	0.133 ± 0.001	0.132 ± 0.001