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Desalting of phenylalanine solutions by electrodialysis with ion-exchange membranes

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Abstract

This paper describes the optimization of the recovery of phenylalanine from an industrial waste stream by electrodialysis. An electrodialysis apparatus, consisting of three compartments equipped with ADP and CDS ion exchange membranes, was tested. These membranes without pretreatment appeared to be less efficient than the first pretreatment membranes which were immersed in a salt waste stream for 18 h. The electrodialysis process with pretreated membranes yielded 87% of recovered phenylalanine. Furthermore, this process has also been successful in removing 98% of salts (Na_2SO_4 and $(NH_4)_2SO_4$), from the initial solution with an average current efficiency in the range of 96%. In the second pretreatment, the membranes were soaked in a bovine serum albumin solution for 2 h before the commencement of the experiment. The results obtained show that the phenylalanine loss is significantly reduced. This loss did not exceed 5% and had an average current efficiency of 98%.

List of symbols

C_i	concentration of the ion i (mol m^{-3})
i	current density (A m^{-2})
t	time (s)
J_i	flux of the ion i (mol m^{-2} s^{-1})
V	volume of the solution in the compartment (m^3)
S	effective area of membranes (m^2)
N_{phe}	molar number of phenylalanine

1. Introduction

Replacement of existing process for amino acid recovery by simple techniques, such as conventional electrodialysis, would be advantageous. Indeed, by using the properties of amino acids, which have different ionic forms (positive, negative and Zwitterion) depending on pH value, the separation and purification of amino acid mixtures have been achieved using electrodialysis techniques [1–6]. Increasing usage of the optical isomer L-phenylalanine in the production of pharmaceutical and food products has led to many studies involving membrane recovery of this amino acid [7–10]. Different membrane techniques have been utilized to extract or separate L-phenylalanine from waste streams. Hong, Choi and Nam [7] have studied the effect of various parameters such as surfactant concentration, agitation speed, carrier concentration and initial sulphuric acid concentration in the interval phase on phenylalanine transport through a liquid emulsion membrane. Peiyan et al. [8] investigated the effect of pH, in the external phase of a liquid emulsion membrane on phenylalanine and aspartic acid transport across this membrane. Hashimoto et al. [9] performed ultrafiltration experiments using solutions which contained bovine serum albumin (BSA) and surfactive agents for the optical resolution of racemic phenylalanine. Extraction of phenylalanine using colloidal liquid aphrons (CLA_S) has been investigated by Scarpello and Stuckey [10]. These authors studied the stability of CLA_S in various aqueous dispersion media and the rates of phenylalanine to and from the solvent phase in the presence of surfactants, and other studies with relevant solutes have been carried out. As for several amino acids, L-phenylalanine produced by the industrial process is mixed with an excess of inorganic salts.

The aim of this work is to recover phenylalanine from a mixture with ammonium and sodium sulfate using electrodialysis with ion exchange membranes. Electrodialysis apparatus equipped with three compartments were utilised with variation of several experimental parameters to determine the optimum conditions of the phenylalanine recovery.

2. Materials and methods

The electrodialysis apparatus consisted of four circulating batch systems in one cell. Each batch system comprised a holding tank with a volume capacity of 200 ml and a circulation pump giving a circulation flow of 3 dm^3 min^{-1}.

The electrodialysis cell, shown in Figure 1, was composed of five compartments divided alternatively with a sulfonic cation exchange membrane (CDS-Morgane Solvay) and a reticuled aromatic quaterned ammonium anion exchange membrane (ADP-Morgane Solvay). The electric resistance was, respectively, 2 and 3 $\Omega\ cm^2$ for CDS and ADP virgin membranes, measured with a 10 g dm^{-3} NaCl solution at 25 °C. The effective membrane area was 51 cm^2. Platinum-coated titanium electrodes were used for both the anode and cathode and have similar surface to ion exchange membranes.

The central compartment was used as a compartment containing a dilute solution where the ions Na^+, SO_4^{2-} and NH_4^+ were transported across the ion exchange membranes. Phenylalanine was prevented from crossing since the experimental pH was in the range of its isoelectric point, pI, that is, this amino acid had a neutral ionic form in this condition. In all compartments, solutions were circulated in the batch mode using Asti pumps.

A synthetic 16.5 g dm^{-3} phenylalanine (SIGMA, Saint Quentin-France) solution containing Na_2SO_4 (40 g dm^{-3}) and $(NH_4)_2SO_4$ (132 g dm^{-3}) salts (Merck, Clevenot, France) was used. This synthetic solution has a similar composition as the industrial waste stream. During electrodialysis experiments, the voltage across the stack, the current density, the pH and volumes and composition in the tanks were measured as a function of time. All experiments were performed at room temperature: 20 ± 4 °C.

The phenylalanine concentrations were determined using an ultraviolet spectrophotometer (Unikon 940-Kontron Instruments) at 256 nm. The sodium ion concentrations were determined by flame photometry using a Hycel pHf 106 photometer. The ammonium ion concentrations were analysed by the Nessler colorimetric method. The sulphate ion concentrations were measured by the nephelometry method using a DR/2000 Hach spectrophotometer.

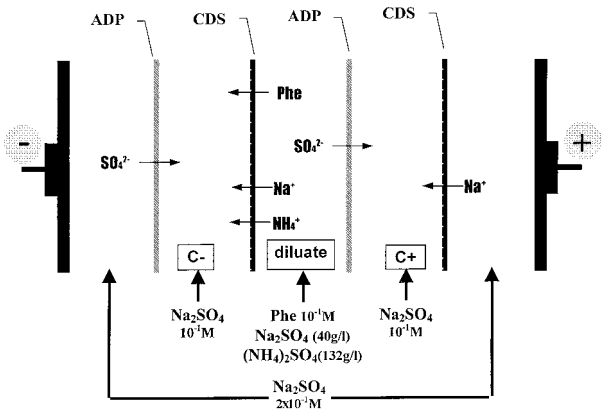

Fig. 1. Schematic representation of the electrodialysis cell: (ADP) anion exchange membrane; (CDS) cation exchange membrane; (Phe) phenylalanine amino acid; (C_+) anionic concentrate compartment; (C_-) cationic concentrate compartment.

3. Results

3.1. *Demineralization of the phenylalanine solution without a membrane pretreatment*

The demineralization of the solution was achieved with ADP and CDS membranes at a current density of 20 mA cm^{-2}. The demineralization process was stopped upon complete removal of salts in the feed compartment (diluate). The evolution of the current density and the applied voltage against the process time indicates that the current density strongly decreased after 13 h, while the applied voltage increased rapidly just after 12 h (results not shown). These results may be explained by an increase in the resistance of the solution resulting from the demineralization of salts in the diluate. Thus, the necessary experimental time retained for the demineralization process was between 12 and 14 h.

A practically constant pH in the diluate during the first 6 h followed by a slight increase during the following 8 h was observed. The change in the concentration of phenylalanine, sodium, ammonium and sulphate ions in the diluate during the demineralisation process is shown in Figure 2. The loss of phenylalanine reached 25% in the feed compartment after only 10 h of the demineralisation process.

The electrodialysis process at this stage had removed not more than 68% of the salts. These performances are not beneficial for industrial applications.

3.2. *Demineralization with pretreated membranes*

3.2.1. *Demineralization with the first pretreatment*

To diminish the loss of the phenylalanine, the ion exchange membranes ADP and CDS were immersed for 18 h in a phenylalanine solution containing $(NH_4)_2SO_4$ and Na_2SO_4. These pretreated membranes were utilized for the demineralization of the phenylalanine solution.

The results obtained, presented in Figure 3, show that the loss of phenylalanine was less than that in the previous experiment without pretreatment. Indeed, the percentage loss of phenylalanine was no greater than 13% after 14 h, that is, at the end of the demineralization process. The evolution of different compounds in the feed compartment during the demineralization process (Figure 3) confirms the total removal of salts (Na^+, NH_4^+ and SO_4^{2-}) after 14 h. The determination of the phenylalanine concentration in all compartments (Figure 4) during the demineralization process showed that the small percentage of phenylalanine transported

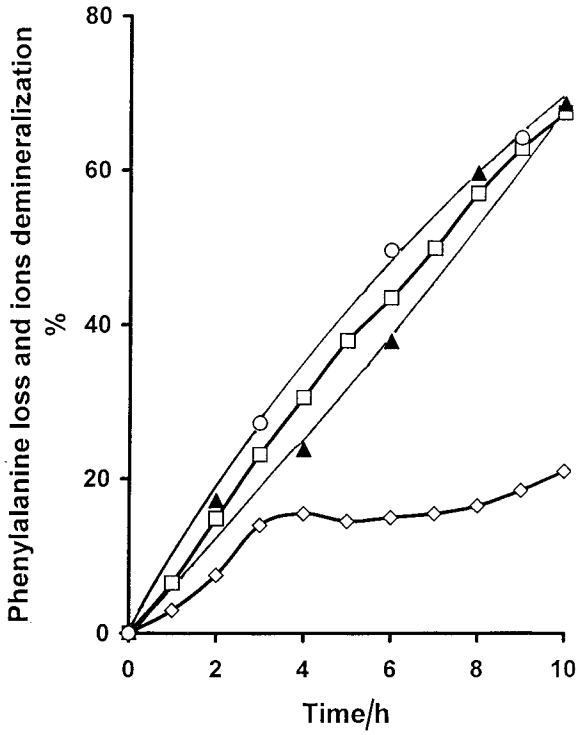

Fig. 2. Demineralization process with ADP and CDS electrodialysis membranes without pretreatment. Conditions: $I = 20$ mA cm^{-2}, $T = 25\,^{\circ}$C and pH 5.3. Key: (◇)% Phe, (□)% Na^+, (▲)% SO_4^{2-}, (○) NH_4^+.

across the ion exchange membranes was mainly found in the cathodic concentration compartment (7.5%). No more than 4% of the phenylalanine electrotransported across the membranes were in the anodic concentrate compartment. Losses of amino acids in the feed compartment were not found in the concentrate compartments C_- and C_+. This discrepancy may be explained by the combined action of adsorption and membrane fouling phenomena. In fact, the determination of the value the electric resistance of the membrane indicates

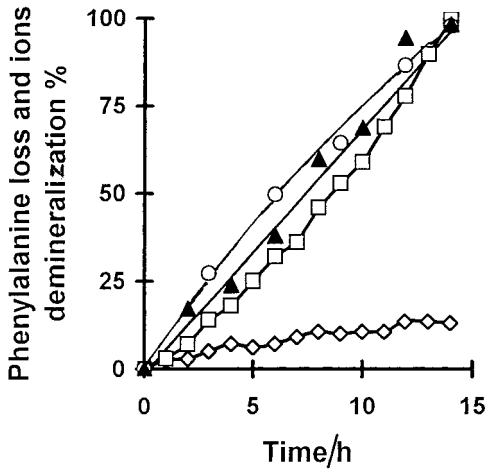

Fig. 3. Loss of phenylalanine and salts in the diluate during demineralization. Conditions: $I = 20$ mA cm^{-2}, $T = 20\,^{\circ}$C and pH 5.3. Key: (◇)% Phe, (□)% Na^+, (▲)% SO_4^{2-} and (○) NH_4^+.

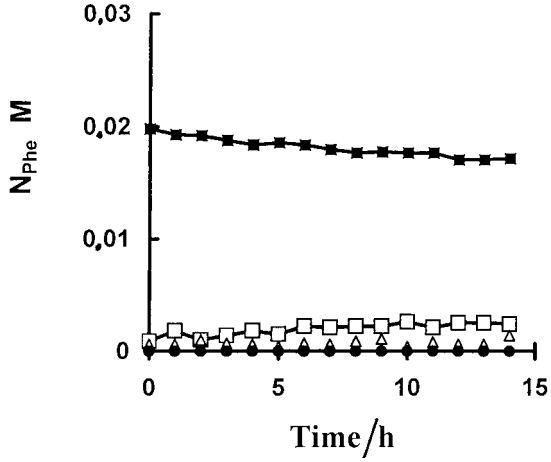

Fig. 4. Change in phenylalanine in all electrodialysis compartments. Conditions: $I = 20$ mA cm^{-2}, $T = 20\,^{\circ}$C and pH 5.3 (in diluate). Key: (■) diluate, (□) anodic concentration compartment, (△) cathodic concentration compartment and (●) electrode compartment.

that the resistance of the ADP and CDS membranes was greater than that of virgin membranes. For the CDS membranes the resistance increased from about 2 Ω cm^2 to approximately 3.7 Ω cm^2. An increase in electric resistance also occurred for the ADP membranes (from 3 to 3.9 Ω cm^2). Previous studies have established fouling of the membranes by amino acids [12, 13].

The fluxes of ionic species through ADP and CDS membranes were calculated using Equation 1:

$$J_i = \frac{V}{S}\frac{\mathrm{d}c}{\mathrm{d}t} \tag{1}$$

The phenylalanine electrotransport was mainly released, in its positive ionic form, across the CDS membrane. The fluxes of NH_4^+ and SO_4^{2-} during the demineralization experiments were about 5 and 3.9 mol m^{-2} h^{-1}, respectively. Although the ionic flux depends on both ionic concentration and mobility, the ratio of these fluxes is in the same range as the ratio of the ionic mobility [11] of sulphate and ammonium ions in the aqueous phase, 7.60×10^{-8} m s^{-1} V and 8.27×10^{8} m s^{-1} V, respectively. The current was mainly carried by the SO_4^{2-} and NH_4^+ ions in the first step. The sodium, which has less mobility (5.19×10^{-8} m s^{-1} V) than NH_4^+ ions, gave a low flux (1.65 mol h^{-1} m^{-2}) through the CDS membrane. With the same ionic concentration in the solution, the electrotransport through a cation exchange membrane of NH_4^+ and Na^+ ions mainly depends on ionic mobilities as recently demonstrated by Bardot, Gaubert and Yaroshchuk [14].

Donnan dialysis of phenylalanine through ADP and CDS membranes was carried out. The experiment operated under similar experimental conditions for the demineralization process with not a voltage applied between the electrodes. Phenylalanine diffused under a concentration gradient from the feed compartment to the concentrate compartments (C_+) and (C_-). The experiment was performed over a period of 14 h and

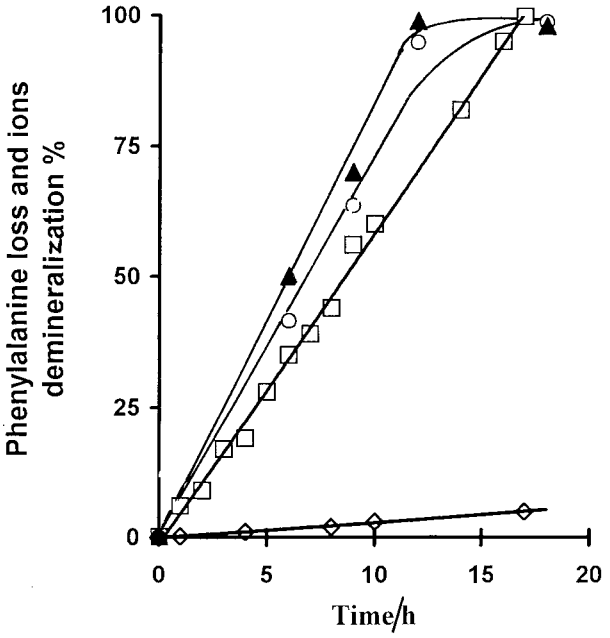

Fig. 5. Change in phenylalanine concentration during demineralization with immobilized BSA electrodialysis membrane in diluate. Conditions: $I = 20$ mA cm^{-2}, $T = 20$ °C and pH 5.3. Key: (◇)% Phe, (□)% Na^+, (▲)% SO_4^{2-} and (○) NH_4^+.

the losses of phenylalanine produced by Donnan dialysis were approximately 3.5% and 2.5% for CDS and ADP membranes, respectively. Thus, the fraction of phenylalanine electrotransported across an ion exchange membrane is acceptable by the industrial users. Furthermore, the phenylalanine was recovered up to 87% from its sodium and ammonium salts solution with high current efficiency of approximately 96%.

3.2.2. *Demineralization with the second pretreatment*

A second pretreatment involved the utilization of a BSA (Sigma, Saint Quentin, France) solution which, by adsorption onto ADP and CDS membranes, created new retention sites to the phenylalanine. Serum albumin is known to have a high affinity binding site for phenylalanine [9]. Immobilized BSA electrodialysis membranes were prepared by circulating BSA solution (10 g dm^{-3}) in the feed compartment for 2 h. It was found that the immobilized BSA membrane showed an efficient demineralization process (Figure 5), with a recovery of practically 95% of phenylalanine from its sodium and ammonium salts. Furthermore, this process has also successfully removed salts (Na_2SO_4 and $(NH_4)_2SO_4$) from the initial solution. An average current efficiency of about 98% was attained.

4. Conclusion

Electrodialysis with ion exchange membranes ADP and CDS appears to be a very interesting and promising technique to extract phenylalanine from industrial waste streams. Adsorption of BSA onto ADP and CDS membranes gave an increased recovery of phenylalanine. Indeed a maximum phenylalanine recovery of 95% was obtained with a 98% demineralization. The current efficiency for the demineralization process was approximately 98%.

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