Separation and Purification Technology 151 (2015) 1–13

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Lactic acid recovery by microfiltration using niosomes as extraction agents

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ARTICLE INFO

Article history:
Received 26 March 2015
Received in revised form 1 July 2015
Accepted 8 July 2015
Available online 10 July 2015

Keywords:
Niosomes
Lactic acid
Span 80
SDS
Microfiltration

ABSTRACT

Lactic acid recovery from dilute aqueous solutions by microfiltration using niosomes of Span 80 (sorbitan monooleate) modified by SDS (sodium dodecyl sulfate) as extraction agents was studied. Experiments were conducted at a transmembrane pressure of 0.3 bar using a 0.20 μm pore size TiO_2 microfiltration flat-disk membrane. The effect of the feed composition (lactic acid concentration, pH, dispersed phase volume, and SDS content in niosomes) on the extraction rate and extraction degree at the equilibrium conditions, and membrane behavior during the subsequent concentration stage were investigated. SDS contained in niosomes, SDS to lactic acid molar ratio in the dispersion, and pH were the main factors affecting the lactic acid extraction degree. The best conditions were achieved with niosomes formulated with Span 80 (20 mol/m^3) and SDS (4 mol/m^3), a SDS to lactic acid molar ratio of 0.010, and pH lower than the pKa of the lactic acid: 33% of lactic acid extraction degree at the equilibrium and a constant permeate flux of 26 L/m^2 h was kept during the dispersion concentration. A two-step process increased the extraction degree up to about 43%. Back-extraction was made by NaOH addition until a pH > 12, where niosome breakup was observed.

1. Introduction

Several plant effluents from pharmaceutical, pulp and paper, and petrochemical industries contain organic acids of low molecular weight, whose recovery may be highly profitable notwithstanding their low concentration. Among them, lactic acid has a paramount importance in biotechnology and food industry, where is used as a food preservative, acidulant, flavoring agent and pH buffer [1,2], and also as a substitute for glycerin in the cosmetics sector. Further fields of applications, such as the production of biodegradable polymers derivatives of polylactic acid (PLA), 'green' solvents from lactate esters, and fine chemical commodity [3,4] reveal the potential of lactic acid and its importance on the chemical market. It is usually obtained by biotechnological fermentation using lactic acid bacteria [5–7] and its recovery from fermentation broths is mainly made by precipitation with calcium hydroxide or by solvent extraction [8,9]. Continuous lactic acid removal by membrane based processes has been shown to effectively increase lactic acid productivity [10]. Although several organic solvents containing the tertiary amine Alamine 336 [11], the secondary amine Amberlite LA-2 [12], tri-n-octylamine or tributylphosphate [13,14] have been studied for efficient lactic acid reactive extraction, an economical method for lactic acid recovery from the fermentation broth is still needed.

Micellar-enhanced ultrafiltration (MEUF) is an alternative process that can be used for organic acids recovery. The surfactant forms large amphiphilic aggregate micelles when added to aqueous streams at a concentration higher than its critical micellar concentration (CMC). The solutes can be retained after being trapped by the micelles, whereas the untrapped species readily pass through the UF membranes. In previous works we studied the recovery of several biocompounds including lactic acid and citric acid with SDS (sodium dodecyl sulfate) by MEUF [15,16]. These processes are considered to be clean technologies as they have the advantages of large-scale continuous separation without phase change, avoiding the use of organic solvents.

In this work we explore the use of niosomes as lactic acid extraction agents, a new technology that so far, to our knowledge, has not been explored. Niosomes or non-ionic surfactant vesicles are formed by one or more surfactant bilayers enclosing an aqueous inside cavity: both hydrophilic and hydrophobic compounds can be encapsulated inside their core and in the bilayer, respectively. Niosomes are preferred to liposomes because of their greater chemical stability, high purity, low cost, content uniformity, and their easy handling and storage [17,18]. Moreover, their large-scale production without using unacceptable solvents is uncomplicated, so they are widely

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http://dx.doi.org/10.1016/j.seppur.2015.07.018
1383-5866/

Nomenclature

C	concentration of species (mol/m^3)
EE_A	lactic acid extraction efficiency (Eq. (1))
HL	lactic acid protonated species
J_p	permeate flux (L/m^2 h) (Eq. (3))
Ka	forward overall volumetric mass-transfer coefficient referred to the aqueous phase (Eq. (7))
Ka_b	backward overall volumetric mass-transfer coefficient referred to the aqueous phase (Eq. (14))
K_{HL}	equilibrium coefficient for the extraction reaction of the lactic acid protonated species (Eq. (11))
K_{L^-}	equilibrium coefficient for the extraction reaction of the anion lactate (Eq. (12))
L^-	lactate anion
P_A	equilibrium distribution coefficient for the lactic acid (Eq. (2))
$SDS_{(NS)}$	molar ratio between the SDS bind to niosomes and the initial added as dispersed phase (Eq. (5))
$SDS_{(m)}$	molar ratio between the SDS adsorbed in the membrane and the initial added as dispersed phase (Eq. (6))
SDS/A	molar ratio between the SDS added in the dispersed phase and the lactic acid content in the initial aqueous phase
t	time (min)
V	volume (cm^3)
VCR	volume concentration ratio (relationship between the feed volume and the retentate volume)
$X_{A(NS)}$	molar ratio between the lactic acid extracted in niosomes and the total amount present in the final retentate after the concentration stage (Eq. (4))
$X_{SDS(NS)}$	molar ratio between the SDS linked to the niosomes and the total amount present in the retentate

Subscripts

A	lactic acid
d	dispersed phase
eq	equilibrium conditions
F	feed dispersion
m	membrane
NS	niosomes
p	permeate
r	retentate
S	total surfactant (Span 80 and SDS)
SDS	sodium dodecyl sulfate
w	aqueous phase

Superscripts

0	initial conditions

used in pharmaceutical, cosmetic and, to a lesser extent, food applications [19–23]. Another advantage for industrial production of these vesicles is the large number of non-toxic and relatively low-cost non-ionic surfactants available for niosome formulation [24]. Encapsulation efficiency depends mainly on niosome structure, the nature and size of the hydrophilic head and the length of the hydrophobic group of surfactant forming the bilayer, pH and composition of the formulation medium, and the nature of the solute [25–27]. Several additives can be added to the formulation in order to stabilize the niosomes. Cholesterol is the most used among them, because of its ability to modify the mechanical strength of the bilayers and their permeability to water [28,29].

In a recent previous work [30] the effect of different formulations containing Span 80 (sorbitan monooleate) as the encapsulating surfactant, cholesterol and SDS as membrane modifiers, and lactic acid as loaded solute has been investigated. Results revealed that SDS acts as a niosome stabilizer that can be used as a substitute of cholesterol because it increased the zeta potential absolute value while decreased the particle size. Additionally, SDS also increased the lactic acid entrapment efficiency, which indicates that Span 80 niosomes modified with SDS can be used as selective extraction agents for the lactic acid recovery when it is in aqueous solutions at low concentration. Based in previous results, this work aims to investigate the potential use of niosomes formulated with Span 80 and SDS as extraction agents of lactic acid in aqueous solution, and the simultaneous separation and concentration of dispersions using flat-disk ceramic microfiltration (MF) membranes. Kinetics and equilibrium capacities of niosomes for lactic acid extraction under different medium conditions are investigated in this work, in order to achieve acceptable levels of lactic acid extraction from dilute aqueous solutions.

2. Materials and methods

2.1. Chemicals

DL-lactic acid (>90% purity, Fluka) was used as solute. The non-ionic surfactant sorbitan monooleate (Span 80, Sigma–Aldrich), with a hydrophilic–lipophilic balance value (HLB) of 4.3 [23], and the anionic surfactant sodium dodecyl sulfate (SDS, 99%, Sigma–Aldrich), with CMC value of 8.3 mol/m^3 [15,16], were used in the formulation of niosomes. Other chemicals such as methanol (HPLC grade, HiPerSolv Chromanorm), maleic acid (>99%, Fluka), phosphoric acid (>85%, Sigma–Aldrich), disodium hydrogen phosphate dodecahydrate (>98%, Panreac), potassium dihydrogen phosphate (>99.5%, Merck), sodium hydroxide (analysis grade, Scharlau), and phenolphthalein (99%, Panreac) were used throughout the experiments. For the determination of SDS the following chemicals were used: ethyl violet (99%, Sigma–Aldrich), glacial acetic acid of analysis quality (Panreac), sodium acetate for analysis (Merck), anhydrous sodium sulfate for analysis (Scharlau), toluene (>99.5%, AnalarNormapur VWR Chemicals) and ethylenediaminetetraacetic acid (EDTA, >99%, Sigma–Aldrich).

Ultrapure deionized Milli-Q water (Millipore, USA) was used for the preparation of all solutions.

2.2. Niosome preparation

Aqueous solutions of single surfactants of Span 80 and SDS were prepared 24 h before their use, in order to hydrate and relax the carbonated chains of their molecular structures, weighing out the exact amounts of surfactant on an analytical balance (Sartorius, accurate to ±0.0001 g), and deionized water addition up to a final volume of 100 cm^3. Niosomes were prepared by direct ultrasonication of 10 cm^3 aqueous solutions of Span 80 (20 mol/m^3) and SDS (0, 2, and 4 mol/m^3), formulated by mixing appropriate volumes of the single surfactant solutions, in round-based polystyrene tubes, 115 mm in height and 29 mm in diameter, supplied by Labbox (Spain). These concentrations were chosen on the basis of the previous results obtained in our laboratory where synergism for lactic acid entrapment was obtained for formulations of Span 80 and SDS with a SDS molar fraction lower than 0.4 [30].

The application of ultrasounds was carried out over a 5-min effective time, with pulses every 5 s (5 s on and 5 s off, 60 cycles; 30% amplitude, 500 W), to avoid overheating of the sample, using a high-intensity ultrasonic processor (Vibra-Cell VCX 500, Sonics