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Flux and retention behaviour of nanofiltration and fine ultrafiltration membranes in filtrating juice from a green biorefinery: A membrane screening

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Abstract

Nanofiltration (NF) of silage juice from a green biorefinery was investigated as a first step to purify lactic acid and amino acids which are seen as valuable products. The performances of three organic NF membranes (PES10, N30F and MPF36) as well as one ultrafiltration (UF) membrane (PES004H) were compared by experiments in a stirred batch cell. Cross flow trials with two inorganic membranes (UF Tami, NF Inocermic) completed the membrane screening. Special attention was directed to the retention of free amino acids, lactic acid, sugars, salts and colouring substances. Nanofiltration showed average fluxes of up to 6.5 L m^{-2} h^{-1}. Decolouring amounted to 80–99%. The membrane screening resulted in a recommendation for one NF membrane (PES10) with adequate specific separation properties. The UF membrane PES004H showed high transmission properties for amino acids and lactic acid in combination with noticeable specific separation properties for colouring substances.

Keywords: Nanofiltration; Green biorefinery; Silage juice; Amino acids; Lactic acid; Inorganic salt

1. Introduction

A green biorefinery is an integrated concept to utilize green biomass as an abundant and versatile raw material for the manufacture of industrial products. This concept is currently in an advanced stage of development in several European countries. Especially unused grassland biomass offers the potential to develop new products from renewable raw materials with a high market potential. Besides biobased materials, energy (via biogas generation) may be supplied by this technological system. As grassland biomass does not offer a specific major component, like sugar beet (sucrose) or corn (starch), it is compelling to establish a multi-product system (Biorefinery system). A key element in the Austrian concept is the utilization of fermented leaf material from clover, alfalfa and grass (grass silage) instead of fresh matter. During the fermentation process, sugar is converted into lactic acid and proteins are hydrolysed into free amino acids. Therefore, lactic acid and amino acids are seen as the key compounds in such a green biorefinery system based on grass silage [1].

However, nanofiltration (NF) is considered as an important unit in the down-stream processing of lactic acid and amino acids. After pressing the grass silage, a brownish silag-juice containing a high amount of lactic acid, inorganic salt, free amino acids and sugars is obtained. A complex down-stream process chain consisting of, e.g. electrodialysis [2,3] and ion exchange/chromatography is expected to separate the valuable substances lactic acid and free amino acids effectively. Especially, for electrodialytic process natural organic matters

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could cause blockage of membranes [4]. Therefore, nanofiltration could be one of the best promising methods to solve that problem.

Nanofiltration is a membrane separation technology classified between ultrafiltration (UF) and reverse osmosis and is used in a wide range of applications. Substances with molar masses higher than ~300 g mol^{-1} and multivalent ions are (partially) retained by NF membranes. In drinking water production, NF is used to remove pesticides and organic matter [5]. Other applications are known in the fields of waste water treatment [6,7], textile industry, tenside industry, biotechnology and food industry [8]. In patent WO 02/053781 [9], an application regarding the recovery of xylose from spent liquors and the recovery of betaine from sugar beet pulp extract is described. Herein, nanofiltration is used to separate molecules like xylose (150 g mol^{-1}) or betaine (127 g mol^{-1}) from larger molecules like glucose (180 g mol^{-1}) or sucrose (342 g mol^{-1}).

As silage juice is a complex mixture, the separation of valuable products like lactic acid and free amino acids is a technological challenge. NF processes offer specific advantages and could be an important part of the process chain to separate lactic acid and amino acids. On one hand, substances larger than approximately 300 Da can be removed in one step which would reduce problems like fouling or other specific problems in subsequent techniques such as, e.g. electrodialysis or chromatography. On the other hand, the more compounds like sugars, small peptides and minerals are separated in the NF step the more it can be assumed that the feasibility of further purification steps can be increased.

It is known that retention characteristics of membranes depend not only on molecular weight of the solutes. Properties like charge and hydrophobicity will also affect the retention of amino acids [10–13] and lactic acid. However, before conducting the comprehensive experiments presented in this paper, no specific literature existed how amino acids would behave during nanofiltration by application of a complex feed like silage juice. In this context, advanced analytic efforts were made to determine the transfer of all substances (amino acids, carbohydrates, cations, anions, organic acids, organic nitrogen and dry matter) during filtration. Additionally, the degree of decolouring was measured by the authors.

2. Material and methods

2.1. Membranes

The organic NF membranes applied in a stirred batch cell were PES10 and N30F (purchased from Nadir, Germany) and MPF36 (Koch, Germany). The organic UF membrane used in the stirred batch cell experiments was PES004H (Nadir, Germany). Ceramic membranes used in cross flow experiments were purchased from Tami (Germany, 23 channels, 0.35 m^2) and Inocermic (Germany, 500 Da, single channel, area 110 cm^2, tube diameter 7 mm). The detailed properties of all membranes are shown in Table 1.

One criterion which can affect flux performance is permeability. In Table 1, it is shown that ceramic membranes have a higher permeability than organic membranes at same NMWCO. The tightest membrane (N30F) showed the lowest permeability.

2.2. Silage juice—feed preparation

Silage juice was prepared by pressing ensiled forages from different sources. Mixing of different silage juices leaded to the feed for the nanofiltration experiments. However, main compounds were red clover (*Trifolium pratense*) and ray grass (*Lolium perenne*). The pressed juice had pH 4. By adding potassium hydroxide up to pH 8.5 phosphate salts were precipitated. Insoluble salts and cell wall materials were removed by centrifugation. Hereafter, a silage juice as specified in Table 2 was obtained. All experiments described in this paper were carried out with this silage juice.

2.3. Experimental apparatus and procedure

2.3.1. Stirred cell experiments

Most organic NF membranes are available as spiral wound modules used in cross flow mode. For testing and screening, flat sheets membranes (the same type which are wounded in large scale spiral wound modules) are used. The experiments were carried out in a stirred cell made of stainless steel (see Fig. 1). The membrane active area (flat sheet type) was 152 cm^2. The assays were conducted in batch mode. The cell was filled with 1000 mL silage juice as feed. The

Table 1
NF and UF membranes used in the experiments

	PES10	N30F	MPF36	PES004H	Inocermic	Tami-1k
Producer	Nadir	Nadir	Koch	Nadir	Inocermic/D	Tami
Material	Ph-PES	Ph-PES	Unknown	Ph-PES	TiO_2	TiO_2
NMWCO (Da)	~1000	~150–350	~1000	~4000	~500	~1000
Pure water permeability at 20 °C ($L\,h^{-1}\,m^{-2}\,MPa^{-1}$)	95[a]	13[a]	60[a]	77[b]	131[b]	240[b]
pH operating range	0–14	0–14	1–13	0–14	0–14	0–14
Maximum temperature (°C)	95	95	70	95	>100	>100
Classification	NF	NF	NF	UF	NF	UF

ph-PES, permanent hydrophylisated Polyethersulfon; NMWCO, Nominal molecular weight cut off.
[a] 1 MPa (10 bar); 20 °C.
[b] 0.2 MPa (2 bar); 20 °C.