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Utilization of enzymatic detergents to clean inorganic membranes fouled by whey proteins

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Abstract

In this work inorganic membranes used for whey protein fractionation were cleaned with enzymatic detergents. The inorganic membrane Carbosep® M1 (Orelis S.A., France), of 150 kg/mol molecular weight cut-off and ZrO_2 filtering layer, was used and the commercial detergent P3-Ultrasil® 62 (Henkel Ibérica S.A., Spain) was selected for the cleaning. Hydraulic and chemical methods were considered to characterize the membrane cleanliness. Cleaning efficiency was observed to be a function of the operating conditions: recycling versus non-recycling of permeate, cleaning solution pH, enzymatic agent concentration and cleaning time. The optimum conditions to perform the cleaning were related to the optimum conditions to hydrolyze whey proteins in a batch reactor. Very high cleaning efficiencies (∼100%) were reached in short operating times (20 min). However, residual matter was detected on the membrane surface after the cleaning.

Keywords: Inorganic membranes; Enzymatic cleaning; Whey protein solutions; Hydraulic cleanliness; Chemical cleanliness

1. Introduction

For a long time proteases have been considered as being very useful ingredients in modern detergents [1]. The idea of using enzymes in detergents was first described by Röhm in 1913 [2]. At that time, only pancreatic enzymes were available and they were not granulated or otherwise protected by physical means. Therefore the storage ability, long-term efficiency and other health aspects were unsatisfactory [3]. The development of enzymes of microbiological origin started in the 1950s with the production of BIO40. This formulation contained a bacterial protease, what was a significant improvement compared to the previous pancreatic products; however the detergent had the disadvantage of a neutral pH [4].

During the 1970s a new generation of high active alkaline detergent enzymes were developed and passed through different generations of physical forms (powders, pills and encapsulates) [5]. The modern technologies (recombinant DNA, genetic engineering and protein engineering) were first applied in 1988 to produce Lipolase™ [4]. Although proteases are still used as one of the main enzymes in detergent formulations, α-amylases, cellulases and lipases are now successfully applied in household laundry detergents, industrial laundering and machine dishwashing.

In membrane technology, a very important research goal is the development of non aggressive cleaning methods able to increase the lifetime of membranes and the proposal of short cleaning times [6]. The use of enzymatic cleaners is of interest because they operate in mild conditions, which is a determining factor for their application to the cleaning of membranes sensitive to chemicals, pH and/or temperature [7,8]. Enzymatic agents can improve the cleaning efficiency and reduce the amount of chemicals needed and the energy costs by working at a lower temperature. Moreover, they are biodegradable and the preparation of tailor-made cleaners is possible. Enzymatic formulations were used by several authors to clean organic membranes [9–11]. However, they reported low cleaning efficiencies and extended cleaning times.

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Nomenclature

a	enzymatic activity (u)
A_m	membrane area (m^2)
cp	cleaning parameter (u/m)
E_{RW}	cleaning efficiency
HD	hydrolysis degree
J	permeate flux (L/h m^2)
J_{wi}	initial water flux (L/h m^2)
n	number of peptidic linkages hydrolyzed per unit of substrate mass
n_{tot}	number of peptidic linkages per unit of substrate mass
ΔP	transmembrane pressure (MPa)
R	membrane hydraulic resistance (m^{-1})
R_c	hydraulic resistance during the cleaning process (m^{-1})
R_{cw}	hydraulic resistance of the cleaned membrane (m^{-1})
R_f	resistance due to membrane fouling (m^{-1})
R_{if}	resistance due to irreversible fouling (m^{-1})
R_m	intrinsic hydraulic resistance (m^{-1})
R_{res}	residual hydraulic resistance (m^{-1})
R_{rf}	resistance due to reversible fouling (m^{-1})
R_{uf}	total resistance of the fouled membrane (m^{-1})
V	volume of cleaning solution (m^3)

Greek letters

μ	dynamic viscosity (Pa s)
ν	kinematic viscosity (m^2/s)
ρ	density (kg/m^3)

The results reported in this paper refer to the cleaning of inorganic membranes used for whey protein fractionation. The feed material is a whey protein concentrate (WPC) with low mineral and residual fat content. Therefore proteins are expected to be the main compounds contributing to membrane fouling [12,13]. In a previous paper by the authors [14], several enzymatic and non-enzymatic commercial detergents were used to hydrolyze whey proteins in a discontinuous reactor. It was concluded that only the enzymatic detergents were able to produce a significant hydrolysis of whey proteins. The best results were achieved with P3-Ultrasil® 62 (Henkel Ibérica, Spain) at temperatures between 48 and 52 °C. Higher temperatures resulted in strong enzyme denaturation, thus causing a dramatic decrease of the enzymatic activity. The maximum hydrolysis degree (about 20%) was reached in 20 min. pH was observed to decrease during the process due to the hydrolysis of the proteins [15]. The optimum initial pH was within the range of 10.3–10.8, what led to an average pH of 9.5–10.0. This enzymatic detergent (P3-Ultrasil® 62) was selected for the membrane cleaning in this work.

In this work the membrane cleaning ability of the detergent P3-Ultrasil® 62 was tested. The influence of operating conditions on the cleaning efficiency was studied and the results were compared to those obtained in the batch reactor.

2. Materials and methods

2.1. Feed solutions

Feed solutions were prepared from the powdered WPC Protarmor PS90 (Armor Protéines, Saint Brice en Cogles, France). Protarmor PS90 WPC was produced from acid whey by successive ultrafiltration (UF) and diafiltration (DF) operations. Its composition is shown in Table 1. The rest of the solids are mainly other proteins and peptides, and lactose. According to the manufacturer, the amount of proteins and peptides in this preparation is about 90% (w/w) on dry matter basis. The amount of low molecular weight compounds, such as salts, in this WPC was very low due to the intensive UF and DF steps. The preparation of the solutions from this concentrate was carried out as described in Argüello et al. [14].

2.2. Cleaning solutions

As feed solutions are mainly composed of proteins, a commercial proteolytic detergent was considered as cleaning agent: P3-Ultrasil® 62 (Henkel Ibérica S.A., Barcelona, Spain). This is a commercial formulation that is a mixture of proteases and anionic tensioactive agents. The molecular weight of the proteolytic enzyme contained in this formulation is approximately 25 kg/mol. In some experiments NaOH was added to the cleaning solutions to adjust the pH.

2.3. Experimental set-up

Experiments were performed in a standard ultrafiltration device. The cleaning tests were carried out on a Carbosep® M1 membrane (Orelis, S.A., Saint Maurice de Beynost, France), which is being used for the fractionation of whey proteins. This membrane consisted of a 6 mm internal diameter tube with a ZrO_2 filtering layer on a carbon support. Membranes of 25, 60 and 120 cm length were used. Carbosep® M1 membranes were reported to have a molecular weight cut-off of 150 kg/mol.

Table 1
Composition of the powdered WPC Protarmor PS90

Compound	Concentration (g/kg)
β-Lactoglobulin	500
α-Lactalbumin	100
BSA	16
Immunoglobulin G	18
Fat	<20
Salts	<30