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#### Review

## Membrane technology for the recovery of detergent compounds: A review

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#### ABSTRACT

The food and beverage industry is a great detergent consumer, due to the extreme cleanliness demanded by this kind of industrial activity. Surfactants play an important role in detergent formulations and for this reason a significant part of this review is devoted to their recovery. Membrane technology has been selected as the most promising method for recovering these cleaning agents and, accordingly, the application of membranes for the recovery and reuse of waste cleaning solutions constitutes another important part of this review. Finally, several studies on the application of membrane technologies for the separation of surfactant compounds are also described.

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#### 1. Introduction

Cleaning and disinfection operations play an important role in food and beverage industries ensuring the safety and hygiene standards currently required by regulation. Cleaning-in-place (CIP) technology is the designation applied to the automatic strategies

employed to reduce the manual work and time devoted to cleaning operations in these industries. The cleaning process in the dairy industry requires between 4 and 6 h per day [1], involving a high consumption of chemicals (caustic soda, nitric acid, surfactants, etc.) and water (since this is the main medium for transporting the chemicals to the soils and the soils from the cleaned surface [2]). Indeed, caustic soda is one of the main compounds used for cleaning in this type of industry, the total quantity drained by a dairy factory processing 10<sup>6</sup> L milk per day amounting to about 120 tons per year [3]. The high volume of effluents containing

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#### Nomenclature

membrane area (m<sup>2</sup>)  $A_{\rm m}$ APG alkyl polyglucose concentration (g/L) feed concentration (g/L)  $C_{\rm F}$ cellulose acetate CA CIP cleaning-in-place

CMC critical micelle concentration COD chemical oxygen demand **EDTA** ethylendiaminetetracetic acid **HTST** high temperature short time **I&I** industrial and institutional sector permeate volume flux (L/h m<sup>2</sup>) I

Κ conductivity (mS/cm)

LABS linear alkyl benzene sulfonates

MF microfiltration

MWCO molecular weight cut-off (Da)

nanofiltration NF

NPE nonylphenol ethoxylate NTA nitrilotriacetic acid

PA polvamide PES polyethersulfone PS polysulfone

recirculation flow rate (m<sup>3</sup>/h)  $Q_{rec}$ retention (%) (e.g.  $R_{COD}$ ) R RC regenerated cellulose Rec recovery (%) (e.g. Rec<sub>NaOH</sub>)

RO reverse osmosis

sodium dodecylbenzene sulfonate **SDBS** 

SDS sodium dodecyl sulfate **SLES** sodium dodecylether sulfate SPD single-phase detergent SS suspended solids Τ temperature (°C) time (h) t

UF ultrafiltration UHT ultra high temperature

cross-flow velocity (m/s) 1) V

volume (L)

VCR volume concentration ratio VRR volume reduction ratio

transmembrane pressure (MPa)  $\Delta P$ 

surface tension (mJ/m<sup>2</sup>) γ

chemicals such as caustic soda or surfactants from the cleaning processes must be treated before leaving the plant in order to recover such chemicals and to avoid environmental pollution. Most surfactants are susceptible to biodegradation and other reactive breakdowns, which may lead to metabolites with significantly different chemical properties [4]. The recycling of waste streams has the advantage that it reduces the need for expensive raw materials and thus the cleaning cost decreases [5]. Furthermore, because of limited water resources, the food industry needs to lower its water consumption and consider the possibility of effluent treatment with a view to water recycling and reuse [6].

Conventional treatment methods for surfactant removal from wastewater include precipitation, adsorption, chemical and electrochemical oxidation, foam fractionation, biological degradation and membrane technology [7,8]. The regeneration of alkaline and acid

cleaning solutions is achieved by decantation, centrifugation, or chemical treatment followed by filtration or membrane operations [9].

Membranes have played an important role as a potentially clean technology for separation and purification purposes. Surfactant separation by membrane processes can be used, for instance, in an industrial plant to recycle most surfactants or at the wastewater treatment plant as a pretreatment process or as a polishing step before the discharge of effluent [10]. This review focuses on the recovery of the cleaning agents (caustic soda and other detergent compounds) by means of membrane technology and discusses methods of recycling in order to reduce cleaning and disinfection costs.

#### 2. Industrial detergent composition

The detergent industry has undergone a substantial transformation in recent years due to the growth of industrial and household consumption, more stringent environmental requirements and the rising cost of energy and raw materials. The current annual 2-3% growth of the detergent industry requires concomitant developments in the formulation of detergents and their methods of application [11]. In general, the principles of wetting, penetrating, lifting, dispersing, suspending and rinsing are applied in most of the cleaning operations in the dairy industry [2]. However, the precise composition (compounds and concentrations) must be optimized for each application depending on the soil that needs to be removed and the surface or material that has to be cleaned. All the ingredients used in household cleaners can also be found in industrial and institutional (I&I) formulations, but some additional I&I ingredients are not suitable for household application [11].

Although detailed formulations of commercial cleaning compositions are not usually made available, it is known that several of those used in food industry cleaning processes include some of the following ingredients:

#### 2.1. Caustic soda

This cleaning agent is commonly used in the dairy industry to dissolve organic soil and many industrial alkaline cleaners contain this agent in their composition. It has good emulsifying properties that prevent the deposition of the soil removed. Potassium hydroxide is another commonly used basic agent.

#### 2.2. Nitric acid

This compound is widely employed to remove mineral scales. Other acid agents like sulphuric or phosphoric acids can be found in some detergent formulations.

#### 2.3. Surfactants

"Surfactant" is an abbreviation for surface active agent. Three concepts need to be considered in order to be able to understand the mechanisms at work in surfactant solutions: solubility, adsorption on a surface and the formation of micelles. The adsorption property is what provides the surface active effects of foaming, wetting, emulsification, dispersion of solids and detergency. The functional effects of emulsification and detergency are also accompanied by the formation of micelles [12]. Surfactants reduce surface tension in water and other liquids through the accumulation of oriented molecules at the interface. This property derives from their amphiphilic structure which includes a hydrophilic head and a hydrophobic tail within the same molecule. The cleaning and dispersant effects of surfactants are due to the aforementioned interfacial activity and it is shown in Fig. 1. Surfactants also find a

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