

The role of surface tension of re-used caustic soda on the cleaning efficiency in dairy plants

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Abstract

During the cleaning in place with recycled cleaning solutions, an increase of suspended solids (SS) and a decrease of the surface tension (γ) of caustic soda (NaOH) solutions were observed for various types of dairy equipment. The decrease of γ was shown to result from the chemical reactions of the milk protein and fat with the cleaning solutions. In this work, the respective roles of SS and γ on the cleaning efficiency, cleanliness and cleaning rate were determined. The cleaning test consisted of an ultrafiltration membrane fouled with skimmed milk and cleaned using four NaOH-based solutions: newly prepared NaOH (high γ), re-used NaOH (low γ) with and without pre-clarification and a newly prepared commercial detergent solution. In the range of γ (28.7–74.0 mJ m⁻²) and SS (0.0–1.7 g kg⁻¹) studied, the cleaning efficiency and the membrane hydraulic cleanliness were similar (0.91–0.94 and 0.69–0.71, respectively). However, it was found that solutions with a low γ resulted in a much faster cleaning rate. The presence of SS was mainly detrimental to the cleaning rate. For an efficient cleaning rate, high pH and low γ were important. A re-used NaOH solution with both low γ and SS was as fast as the commercial detergent solution at the same temperature (50 °C).

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1. Introduction

Cleaning in place (CIP) systems in the dairy industry significantly contribute to the level of water consumption, and to the volume and polluting load of the aqueous effluent invariably produced. They are also mainly responsible for the high pH value (9–11) in the wastewater reaching water treatment stations.

Caustic soda (NaOH) solutions, most commonly used as chemical cleaning detergent on an industrial scale (Henck, 1995), are either discharged after one use (single-use system) or re-used before being discharged and renewed (multi-use and re-use systems; FIL-IDF, 1979; Romney, 1990). The frequency of cleaning solution discharge varies according to the dairy equipment and plants to be cleaned (1 day–1 year), based on subjective criteria (colour, odour).

Recent work (Gésan-Guiziou, Boyaval, & Daufin, 2002; Merin, Gésan-Guiziou, Boyaval, & Daufin, 2002) has shown that re-use of caustic solutions induces a progressive increase in concentration of suspended solids (SS) and of chemical oxygen demand, both total (COD_t) and soluble (COD_s). This causes a decrease in surface tension (γ) of the cleaning solutions, to levels around 30 mJ m⁻² in the course of the cleaning cycles. These γ values are much smaller than that of a newly prepared 2% caustic solution (74 mJ m⁻²). The present work shows that these phenomena, observed in caustic solutions used in several industrial CIP systems, are generated by the chemical degradation of major milk components (proteins, fat) by NaOH.

The cleaning functionality of re-used industrial NaOH solutions, with low surface tension and clarified using microfiltration (MF) or nanofiltration (NF) have been studied with an original methodology based on the cleaning of an ultrafiltration (UF) membrane (Merin et al., 2002). The cleaning efficiency was better and cleaning kinetics were faster with caustic solutions containing both

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low surface tension and no SS (after MF or NF regeneration of the used NaOH solutions) compared with newly prepared NaOH (Merin et al., 2002). However, the specific effect of surface tension and suspended matter have not been distinguished, mainly due to the high variability of industrial caustic solutions tested.

The objective of the present work was to determine the respective contributions of the surface tension and the SS to the functionality of the cleaning, and in particular to the cleaning kinetics.

2. Materials and methods

2.1. Caustic soda solutions

2.1.1. Industrial cleaning in place solutions

Industrial CIP solutions were sampled from several dairy plants (Table 1). The industrial caustic solutions were prepared from technical-grade NaOH either as a 30.5% solution or as pellets (CIP A, Table 1). Tap water from the local source was used in either case.

For single-use CIP systems (A, A' and B) a representative sample was withdrawn from the feed tank at the end of the cleaning performed in a closed loop. For CIP A, two additional samples were withdrawn: one at the beginning and one at the end of the “de-sludging” operation, performed in an open loop prior to the cleaning. The “de-sludging” operation involved the discharging of the largest part of the collected debris during the first stage of cleaning in order to limit the contamination of the NaOH solution.

For the re-use CIP system (C, D, E, F), a representative sample was withdrawn from the caustic solution circulation loop after 1 day of re-use.

2.1.2. Experimental cleaning in place solutions

The NaOH solution (20 g L^{-1}) was prepared from 30.5% technical NaOH (Langlois Chimie, Saint Jacques de la Lande, 35, France) mixed with microfiltered ($0.2 \mu\text{m}$) tap water.

In order to determine the role played by milk components on the important parameters affecting the contam-

ination and regeneration of the NaOH solutions (COD_t , COD_s , SS, γ), the main milk components were put into contact with NaOH in a closed agitated reactor. This methodology overcomes the difficulties of recovering deposited material from fouled industrial equipment surfaces. The reactor of 1 L volume (Pyrex Glass; $10 \text{ cm } \varnothing \times 15 \text{ cm}$) was agitated with a magnetised bar and maintained at a constant temperature of 70°C in a water bath using a Polystat (Bioblock Scientific, Illkirch, 67, France). Milk constituents were derived from different dairy product powders: whole milk (UCLAB, Landerneau, 29, France), skimmed milk (Schuck, Piot, Méjean, Le Graet, et al., 1994) and “native calcium phosphocaseinate”, PPCN, which is a powder composed of $\approx 87\%$ casein micelles (Schuck, Piot, Méjean, Fauquant, 1994). Milk reactant (70 g powdered whole milk, skimmed milk or PPCN) was added into a caustic solution, corresponding to 2.10 g of total nitrogen matter (total Kjeldahl nitrogen (TKN)) and to 2.31, <0.5 and ≈ 0 g fat, respectively. The solutions were maintained at 70°C for 1 h. The compositions of the solutions are given in Table 2. The influence of components resulting from the degradation of lactose (Condat-Ouillon, 1995) was deliberately not studied, since lactose is of minor importance, being totally removed during the rinsing phase of cold circuits (Tissier, Corrieu, & Lalande, 1983) and not present in the fouling deposits observed in heat exchangers (Gallot-Lavallée, Leclerc-Perlat, & Lalande, 1988).

2.2. Evaluation of cleaning performances of alkaline solutions

Four cleaning solutions were compared (Table 3): Ultrasil 13 (Henkel-Ecolab, Issy Les Moulineaux, France), a commercial detergent of low γ , largely used for the cleaning of membrane equipment, fresh NaOH (with no SS, no COD and high γ), and two contaminated NaOH solutions each with a high COD_s and low γ , but one pre-clarified and the other without pre-clarification (i.e., high SS concentration). The concentration of SS and COD_t in the used solutions formulated with whole milk were modified using MF ($0.1 \mu\text{m}$) with permeate circulation

Table 1
Industrial cleaning in place systems studied

Code	Equipment to be cleaned	Process fluid	Cleaning in place (CIP) procedure	
			Single use	Reuse: discharge frequency
CIP A	Pasteuriser	Whole milk	—	—
CIP A'	Milk pipes	Whole milk	—	—
CIP B	Pasteuriser	Cream	—	—
CIP C	Tanks, pipes, cream separator	Whey, whey cream	—	≈ 1 month (colour)
CIP D	Tanks, pipes, cream separator	Whey, whole milk	—	≈ 1 month (colour)
CIP E	Tanks, pipes, pasteuriser	Whole milk, skimmed milk, cream, whey	—	2 months
CIP F	Cheese vats	Whole milk, milk concentrates	—	No discharge

Table 2
Composition (g kg⁻¹) of dairy products and cleaning solutions studied^a

Solvent + reagent		$\gamma^{b,c}$ (mJ m ⁻²)	COD _t ^{b,c} (g L ⁻¹)	COD _s ^{b,c} (g L ⁻¹)	SS ^{b,c} (mg kg ⁻¹)	DM ^{b,d} (g kg ⁻¹)	NCN ^{b,d} (g kg ⁻¹)	NPN ^{b,d} (g kg ⁻¹)	Fat ^d (g kg ⁻¹)	MM ^{b,d} (g kg ⁻¹)	Lactose ^d (g kg ⁻¹)
H ₂ O	Whole milk	43.5±0.8	9.65±0.05	nd	nd	7.85	0.47	0.11	2.31	0.46	nd
H ₂ O	Skimmed milk	49.9±0.1	5.55±0.05	nd	nd	5.62	0.42	0.11	< 0.5	nd	3.06
H ₂ O	PPCN	49.9±0.1	2.65±0.05	nd	nd	2.34	0.11	0.01	0.00	nd	0.05
NaOH 2%	—	74.0±0.2	0.00±0.01	0.00±0.01	0.00±0.01	—	—	—	—	—	—
NaOH 2%	Whole milk	29.8±0.4	8.61±0.06	5.15±0.03	2027±80	—	—	—	—	—	—
NaOH 2%	Skimmed milk	40.8±0.1	5.28±0.06	5.28±0.05	46±10	—	—	—	—	—	—
NaOH 2%	PPCN	42.7±0.1	2.57±0.05	2.53±0.02	300±5	—	—	—	—	—	—

^aSolutions were prepared on the basis of 2.10 g TKN kg⁻¹ (TKN: Total Kjeldahl Nitrogen).

^b γ : surface tension; COD_t, COD_s: total and soluble chemical oxygen demand; SS: suspended solids; DM: dry matter; NCN: non-caseinic nitrogen; NPN: non-proteinic nitrogen; MM: mineral matter; PPCN: phosphocaseinate.

^cValues given as means ± standard deviation of duplicate determinations of two experiments.

^dValues according to calculations performed from industrial powder composition. nd: not determined.

(“bactocatch” system, transmembrane pressure (TP), TP ≈ 0.5 bar, permeation flux, $J \cong 200 \text{ L h}^{-1} \text{ m}^{-2}$, temperature, $T \cong 70 \text{ }^\circ\text{C}$).

The performances of each cleaning solution (in terms of efficiency, cleanliness and rate) were quantified by applying to an UF membrane fouled with skimmed milk, using a procedure described below and initially proposed and used by Daufin, Merin, Labbé, Quémerais, and Kerhervé (1991), Kim, Sun, Chen, Wiley, and Fane (1993) and Gésan, Daufin, Bousser, and Krack (1996).

2.2.1. Operating procedure

The experimental set-up was a filtration loop previously described by Merin et al. (2002). The unit comprised a 5 L feed tank connected to a screw pump (LS 80S3, Moineau, Vanves, France) circulating 200–900 L h⁻¹ at a pressure of 6 bar. Two electromagnetic flowmeters (±0.2%) were installed, one in the retentate compartment (Deltaflux-X1000, Krohne, Dordrecht, The Netherlands) and, one in the permeate withdrawal (MG 711/F-D, Turbo, Köln, Germany). Two pressure sensors (±0.2%) (ED 522/354-239/0/5, Haenni, ATN, Carquefou, 44, France) were installed at the entrance and at the outlet of the membrane module on the retentate side. TP was regulated using a pneumatic valve (Varipak 8013-757, Masoneilan, Condé sur Noireau, France). A heat exchanger (N3 001-4200, Haake N3, Karlsruhe, Germany) was used to maintain the temperature (T) of the fluid inside the filtration loop using a 100 Ω platinum sensor. The data measured (flow, pressure, temperature) were recorded continuously using a data acquisition system (SAM 80-RS, AOIP, Evry, 91, France).

The UF membranes used were Céram 15 kg mol⁻¹, 3 channels (hydraulic diameter: $3.6 \times 10^{-3} \text{ m}$), 1.2 m long, α -alumina with a ZrO₂ and TiO₂ filtering layer, 0.045 m² (TAMI Industries, Nyons, France). The membrane composition allowed performing experiments in extreme physico-chemical conditions, i.e., pH ≥ 13 and T up to 80 $^\circ\text{C}$.

The UF membrane was cleaned and conditioned before and after every experiment using 2 detergent steps (D'Souza & Mawson, 2005): Ultrasil 13 solution (10 g kg⁻¹; $T = 80 \text{ }^\circ\text{C}$; crossflow velocity, $v = 5 \text{ m s}^{-1}$; TP ≈ $0.7 \times 10^5 \text{ Pa}$ for 30 min), followed by a HNO₃ solution (4.9 g kg⁻¹; $T = 55 \text{ }^\circ\text{C}$; $v = 5 \text{ m s}^{-1}$; TP ≈ $0.7 \times 10^5 \text{ Pa}$ for 20 min). The hydraulic resistance of the clean membrane, R_m , was determined by a water flux after membrane rinsing with microfiltered (0.2 μm) tap water. The initial hydraulic resistance of the clean membrane, calculated according to the Darcy's law, was $2.7 \pm 0.1 \times 10^{12} \text{ m}^{-1}$.

After a water rinse of the retentate and permeate sides of the filtration loop, the fouling and cleaning sequences were performed in a closed loop with recycling permeate into the feed tank.

The UF membrane was fouled by filtering thermised (63 $^\circ\text{C}$, 15 s) skimmed milk provided by Entremont (Montauban de Bretagne, 35, France) at the following operating conditions: $T = 50 \text{ }^\circ\text{C}$; $v = 4 \text{ m s}^{-1}$; TP = $1.5 \times 10^5 \text{ Pa}$ for 1 h. The evolution of the overall fouling hydraulic resistance due to skimmed milk, $R_{f(\text{SM})}$, in the course of time made it possible to verify the reproducibility of the fouling step: $R_{f(\text{SM})}$ reached a value of $3.0 \pm 0.3 \times 10^{13} \text{ m}^{-1}$ at the end of the experiment. After a water rinse, the membrane resistance due to irreversible fouling, $R_{if(\text{SM})}$, was calculated from the pure water flux measurements: $R_{if(\text{SM})} = 1.5 \pm 0.4 \times 10^{13} \text{ m}^{-1}$. The fouled membrane was cleaned using each of the prepared cleaning solutions presented in Table 3.

The cleaning cycle applied to the fouled membrane was performed at the following conditions: $T = 50 \text{ }^\circ\text{C}$; $v = 4 \text{ m s}^{-1}$; TP = $1 \times 10^5 \text{ Pa}$ for 1 h. The development of membrane fouling resistance with time, $R_f(t)$, during the cleaning test was calculated according to Darcy's law. After rinsing with water, the cleaned membrane water flux was measured to calculate the resistance due to residual irreversible fouling after the cleaning test, $R_{if(\text{test})}$. Samples of the cleaning solution were withdrawn during cleaning for physico-chemical analyses.

Table 3
Composition and properties of cleaning solutions studied

Cleaning solution	NaOH ^a (g kg ⁻¹)	γ ^{b,a} (mJ m ⁻²)	COD _f ^{b,a} (g L ⁻¹)	COD _s ^{b,a} (g L ⁻¹)	SS ^{b,a} (g kg ⁻¹)	Conductivity ^a (mS cm ⁻¹)	Efficiency ^c (dimensionless)	Cleanliness ^c (dimensionless)	$k^{b,c}$ (10 ⁻¹³ m h ⁻¹)
Ultrasil 13	5.2 ^d	41.0 ± 0.5	1.8 ± 0.1	1.8 ± 0.1	0.00 ± 0.01	32.1 ± 0.5	0.91 ± 0.11	0.69 ± 0.08	24 ± ±2
Fresh NaOH	20.0 ± 0.2	74.0 ± 0.2	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	88.6 ± 1.1	0.92 ± 0.11	0.70 ± 0.08	8 ± 1
Contaminated NaOH without SS	20.4 ± 0.2	33.5 ± 0.2	4.9 ± 0.1	4.9 ± 0.1	0.03 ± 0.01	89.8 ± 1.0	0.91 ± 0.11	0.70 ± 0.08	24 ± ±2
Contaminated NaOH with SS	19.4 ± 0.2	28.7 ± 0.2	7.6 ± 0.1	5.1 ± 0.1	1.70 ± 0.01	84.5 ± 0.9	0.94 ± 0.11	0.71 ± 0.08	13 ± 1

^aValues given as mean ± standard deviation of duplicate trials.

^b γ : surface tension; COD_f: total and soluble chemical oxygen demand; SS: suspended solids; k : kinetic constant for cleaning.

^cVariation of values assessed by taking into account experimental errors and difference between replicates when performed.

^dInformation from Henkel-Ecolab.

2.2.2. Calculated parameters

The performances of membrane cleaning using alkaline solutions were evaluated in terms of three parameters (cleaning efficiency, membrane cleanliness, kinetics constant) defined from hydraulic resistances determined according to Darcy's law (Gésan et al., 1996).

The hydraulic resistance of a membrane, R , was calculated according to

$$R = \frac{TP}{\mu \times J}, \quad (1)$$

where R is the overall hydraulic resistance (m⁻¹), μ the dynamic viscosity of the permeate (Pa s), J the permeation flux (m s⁻¹).

If the membrane is clean, $R = R_m$. During filtration, $R = R_m + R_f$ with $R_f = R_{rf} + R_{if}$ where R_f is the overall hydraulic resistance after fouling, R_{if} the hydraulic resistance due to irreversible fouling, measured after removal of the reversible fouling by water rinse, and R_{rf} the hydraulic resistance due to reversible fouling, all expressed in m⁻¹.

The cleaning efficiency, which represented the relative part of the fouling removed from the membrane by the cleaning process, was expressed as follows:

$$\text{Efficiency} = 1 - \frac{R_{if(\text{test})}}{R_{if(\text{SM})}}, \quad (2)$$

where $R_{if(\text{test})}$ is the hydraulic resistance due to irreversible fouling after the cleaning test (m⁻¹), and $R_{if(\text{SM})}$ is the hydraulic resistance due to irreversible fouling after the skim milk ultrafiltration (m⁻¹).

The hydraulic cleanliness of the UF membrane, which represented the contribution of residual fouling resistance relative to clean membrane resistance was calculated as follows:

$$\text{Cleanliness} = \frac{R_m}{R_m + R_{if(\text{test})}}. \quad (3)$$

The kinetics of the cleaning process was evaluated from the evolution of the fouling hydraulic resistance in the course of cleaning, $R_f(t)$. The evolution of $R_f(t)$ was the result of the simultaneous effects of membrane cleaning and of membrane re-fouling by compounds either initially present in the cleaning solution or which appeared in the cleaning solution in the course of the cleaning process. Using the methodology proposed by Merin et al. (2002) for the treatment of $R_f(t)$ data, it was verified that during the first 10 min (under stationary operating conditions), the cleaning kinetics was mainly attributed to the cleaning effect and not so much to the re-fouling phenomenon; the cleaning kinetics obeyed a second-order reaction ($r^2 \geq 0.9$):

$$\frac{1}{R_f} = kt + \text{constant}. \quad (4)$$

The kinetic constant, k (m h⁻¹), allowed comparison with the cleaning kinetics obtained with the different NaOH solutions tested (Daufin et al., 1992).

The reproducibility of such experiments was previously shown to be good (Merin et al., 2002).

2.2.3. Amount of removed deposit

For the cleaning with fresh NaOH solution, the amount of deposit initially fixed on the membrane was estimated. The deposit amount, M_{total} (kg), at time $t = t_n$ was calculated by numeric integration according to the trapeze method ($\pm 2\%$):

$$M_{\text{total}} = \sum_{i=0}^n M_{\text{removed}}(t_i), \quad (5)$$

$$M_{\text{removed}}(t_i) = \left(\frac{C_{i-1} \times Q_{i-1} + C_i \times Q_i}{2} \right) \times (t_{i-1} - t_i), \quad (6)$$

where C_{i-1} , C_i is the concentration in “protein equivalent”, circulating in the retentate compartment at time t_{i-1} and t_i (kg m^{-3}) and Q_{i-1} , Q_i the retentate flow of the solution at time t_{i-1} and t_i ($\text{m}^3 \text{h}^{-1}$).

The concentration in “protein equivalent” of skimmed milk, C_M , was calculated from the optical density, OD at 254 nm according to (Alvarez, 2003)

$$C_M(\text{mg L}^{-1}) = 713 \times \text{OD} - 22.7 (r^2 = 0.999). \quad (7)$$

Determination of the efficiency and cleanliness of the various cleaning solutions was conducted in duplicates. However, the determination of cleaning rate was not duplicated because the reproducibility was previously shown to be good (Merin et al., 2002). The significance of the difference between results (cleaning efficiency, cleanliness, cleaning rate) from different experiments was assessed by taking into account experimental errors and difference between replicates, if performed: cleaning efficiency ($\pm 12\%$), cleanliness ($\pm 12\%$) and kinetic constant ($\pm 6\%$).

2.3. Analytical methods

2.3.1. Physico-chemical parameters

The following physico-chemical measurements were carried out (the accuracy of the methods is given in parentheses).

Density ($\pm 1\%$) was measured using a densitometer (DM A48 AP Paar, Roucaire, Rennes, France), and dynamic viscosity of Newtonian fluids ($\pm 1\%$) was obtained with a D8 Haake viscosimeter (Karlsruhe, Germany). The conductivity ($\pm 2\%$) was measured with a 660 conductimeter (Metrohm AG 9101, Herisau, Switzerland), and the turbidity ($\leq \pm 10\%$) with a turbidimeter Hach 2100 AN IS (Namur, Belgium) range 0–10 000 NTU (Nephelometric Turbidity Unit). The optical density (OD) (spectrophotometer UVIKON 922, KONTRON Instruments, Milan, Italy) at 254 nm, where NaOH absorption is close to zero, was taken as proportional to the concentration of proteins of the sample (Kuaye, 1994) (accuracy: 0.02). Rigorously, it corresponds to “protein equivalent” since proteins coming from the fouling layers are hydrolysed by OH^- ions during the alkaline cleaning.

Titration of NaOH ($< 2\%$) was performed with HCl (1 N) according to two methods (Alvarez, 2003): (i) titration acid–base with phenolphthalein, and (ii) titration of pH on a dosage bench (Schott Geräte TR155, TA20 and T100, Hofheim, Germany; electrode INGOLD 90 433, Mettler–Toledo, Urdorf, Switzerland). The pH was measured using a pH meter (PHM 80 portable pH meter, Radiometer, Copenhagen, Denmark).

2.3.2. Contamination parameters of the cleaning solutions

The COD of the alkaline solutions was measured by Nanocolor Test 29 cuvettes and a PF 10 pocket filter photometer (Macherey–Nagel, Strasbourg, France). This method was correlated with the results obtained by the French Standard NF T90-101 Afnor (1988) (accuracy $\pm 2\%$) (Dresch, Daufin, & Chaufer, 1999). COD_t was measured in a whole sample, and COD_s was measured in a supernatant after centrifugation ($3000 \times g$, 20 min, 20°C).

SS data ($\pm 10\%$) were determined according to a french Standard (NF T90-105, Afnor 1978) using filtration of 100–500 g of sample on a $1.2 \mu\text{m}$ glass-fibre filter (GF/C, Whatman, Maidstone, United Kingdom) and drying the filter at 105°C overnight.

The surface tension ($\pm 1\%$) was measured at 20°C by a tensiometer (K12, Krüss, Hamburg, Germany) with Wilhelmy plate.

A rapid determination of dry matter (DM), nitrogen matter, fat, lactose ($\pm 2\%$) was performed on raw materials (whole milk, skimmed milk) using the infra-red DairyLab2 apparatus (Foss France SA, 92 Nanterre, France).

The analyses performed for the characterisation of composition and properties of cleaning solutions are given as means of two real repetitions. Each repetition was the mean of two or three measurements performed the same day. The variation in the number of measurements depended on the discarding of some aberrant ones. Results were expressed as a mean value with a standard deviation (σ).

The linear regression between measured parameters were assessed using the Excel Software (Excel version 2000, Microsoft, Seattle, USA).

3. Results and discussion

3.1. Composition of industrial cleaning in place alkaline solutions

The characteristics of industrial cleaning solutions varied within wide ranges: NaOH $1.0\text{--}24.2 \text{ g kg}^{-1}$; COD_t $0.3\text{--}3.9 \text{ g L}^{-1}$; COD_s $0.3\text{--}2.8 \text{ g L}^{-1}$; SS $20\text{--}1760 \text{ mg kg}^{-1}$; turbidity $16\text{--}2020 \text{ NTU}$ (Table 4) reflecting values reported by Henck (1993), Condat-Ouillon (1995), Dresch et al. (1999) and Räsänen, Nyström, Sahlstein, and Tossavainen (2002).

A strong correlation ($r^2 > 0.99$) existed between the NaOH content and the conductivity χ , which was very close to that obtained for the fresh NaOH solutions despite

Table 4
Characteristics of caustic soda solutions withdrawn from industrial cleaning in place systems

Code ^a	$\gamma^{b,c}$ (mJ m ⁻²)	SS ^{b,c} (mg kg ⁻¹)	Turbidity ^a (NTU)	COD _t ^{b,c} (g L ⁻¹)	COD _s ^{b,c} (g L ⁻¹)	NaOH ^a (g kg ⁻¹)	Conductivity ^a (mS cm ⁻¹)
A de-sludging (t = 5 s)	37.4 ± 0.1	2100 ± 42	2150 ± 15	9.03 ± 0.02	6.33 ± 0.01	4.3 ± 0.1	19.5 ± 0.1
A de-sludging (t = end)	45.5 ± 0.1	540 ± 10	510 ± 5	1.61 ± 0.02	1.34 ± 0.01	1.0 ± 0.1	5.0 ± 0.1
A end of cleaning ^d	38.8 ± 0.6	1760 ± 10	2020 ± 1	3.42 ± 0.02	2.31 ± 0.01	5.7 ± 0.1	27.4 ± 0.1
A' end of cleaning ^d	59.0 ± 0.3	85 ± 5	43 ± 2	0.28 ± 0.02	0.28 ± 0.02	8.9 ± 0.1	42.1 ± 0.1
B end of cleaning ^d	31.0 ± 0.2	820 ± 10	1360 ± 12	2.41 ± 0.05	1.01 ± 0.02	17.7 ± 0.1	81.0 ± 0.1
C	51.4 ± 0.5	90 ± 3	80 ± 2	0.45 ± 0.01	0.41 ± 0.01	8.2 ± 0.1	39.5 ± 0.2
C ^e	43.6 ± 0.2	150 ± 11	206 ± 2	0.97 ± 0.03	0.79 ± 0.02	11.4 ± 0.1	53.5 ± 0.1
D	33.7 ± 0.2	20 ± 1	16 ± 4	0.54 ± 0.01	0.52 ± 0.01	16.0 ± 0.1	73.9 ± 0.1
E	27.9 ± 0.2	560 ± 4	850 ± 10	3.88 ± 0.02	2.84 ± 0.03	19.5 ± 0.1	86.7 ± 0.1
F	41.5 ± 0.2	110 ± 2	131 ± 2	0.44 ± 0.01	0.36 ± 0.01	24.2 ± 0.1	106.1 ± 0.1

^aRefer to Table 1 for code explanation.

^b γ : surface tension; SS: suspended solids; COD_t, COD_stotal and soluble chemical oxygen demand.

^cMeans ± standard deviation of duplicate analyses.

^dEnd of alkaline cleaning phase performed in closed loop.

^eAfter cleaning of cream separator.

the large variations of pollutant loads of the different solutions. The conductivity was correlated with the NaOH concentration according to

$$\chi(\text{mS cm}^{-1}) = a \times [\text{NaOH}](\text{g kg}^{-1}) + b$$

with $a = 4.4 \text{ mS kg cm}^{-1} \text{ g}^{-1}$ and $b = 2.3 \text{ mS cm}^{-1}$.

The turbidity was correlated ($r^2 = 0.95$) with SS content according to

$$\text{Turbidity (NTU)} = c \times \text{SS (g kg}^{-1}) + d$$

with $c = 1.1 \text{ NTU kg g}^{-1}$ and $d = 57.6 \text{ NTU}$.

Globally, regardless of the type of dairy equipment and the CIP systems (single use or re-use), the surface tension of the cleaning solution decreased when compared to the value obtained with the fresh NaOH solution, confirming the measurements performed by Henck (1993) and Merin et al. (2002) on re-used solutions. The surface tension decreased sharply from 74.0 mJ m⁻² for a fresh NaOH solution (COD_s = 0 g L⁻¹) to values between 59.0 and 27.9 mJ m⁻² for industrial solutions of COD_s ≥ 0.3 g L⁻¹ (Fig. 1) confirming the tendency reported for a NaOH solution originating from a CIP system of milk standardisation equipment (Gésan-Guiziou et al., 2002). The γ dropped as soon as the cleaning started and the amount of dissolved matter of the NaOH solutions increased simultaneously from around 0.3–0.5 g L⁻¹ of COD_s to a high polluting load of 6.3 g L⁻¹ (Fig. 1).

These results suggest that molecules originating from the alkaline hydrolysis of milk proteins (whether heat denatured or not), and of the fat, have surfactant properties. The higher the soluble COD of the NaOH solution the higher the content of surfactant molecules. The stabilisation of γ in the range 30–40 mJ m⁻² could be caused reaching a certain critical micellar concentration, well known for a given surfactant molecule (Adamson, 1976).

3.2. Cause for surface tension decrease of used caustic soda solutions

The surface tension γ of whole and skimmed milk, 44.3 and 47.5 mJ m⁻², respectively, was in the range reported for whole milk (36.2–56.7 mJ m⁻²) and slightly higher for skimmed milk (48.2–56.6 mJ m⁻²) (Michalski, Desobry, & Hardy, 1997). Dissolving those raw materials and the native phosphocaseinate (PPCN) in water, at a final TKN concentration of 2.1 g kg⁻¹, did not change the γ value significantly (Table 2): 43.5 mJ m⁻² for diluted whole milk; 49.9 mJ m⁻² for diluted skimmed milk and PPCN. However, dissolving whole milk, skimmed milk and PPCN in NaOH yielded a strong γ decrease, indicating that products of the reaction of NaOH with both proteins and fat were responsible for γ decrease. With the same TKN concentration (2.1 g kg⁻¹), the decrease of γ depended on the amount of fat present (Table 2). But the quantification of the relative contributions of caseins, soluble proteins and pure fat on the decrease of γ needs further experiments with each type of components.

The results obtained are comparable to those of Friis, Simon, Emborg, and Olsen (1998) who reported γ decrease from >45 to <30 mJ m⁻² after a few minutes cleaning of a milk-fouled pasteuriser when using an enzyme-based detergent solution with proteases and lipases ([0.06–0.12%], pH > 8). The phenomenon is attributed to in situ hydrolysis of fat and proteins which produce surfactant molecules; fat would be mainly responsible for the phenomenon since surface tension with whole milk was significantly lower than with skimmed milk and PPCN (Table 2). Saponification of lipids by NaOH with the formation of glycerol and the sodium salts of fatty acids (soaps) is known to be a slow reaction: only 34% of fat is saponified after 8 h reaction ([fat] = 0.5 g L⁻¹,

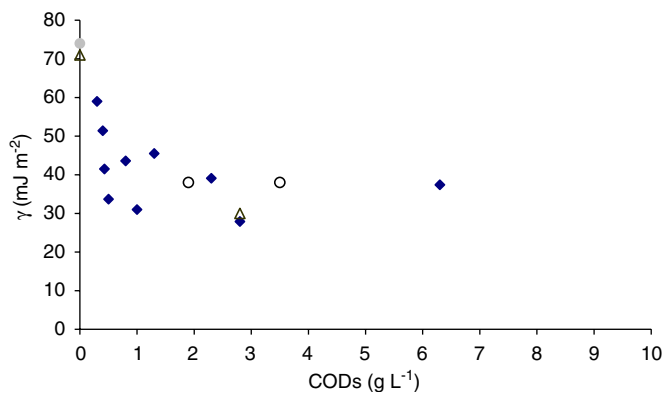


Fig. 1. Reduction of surface tension γ as a function of soluble chemical oxygen demand, (COD_s) of industrial NaOH solutions (◆). Comparison with fresh NaOH solution (○) and with data from Merin et al. (2002) (△) and from Henck (1993) (○). See Tables 1 and 4 for composition of industrial NaOH solutions.

NaOH = 2%, $T = 80^\circ\text{C}$) according to Condat-Ouillon (1995). The saponification kinetics is also known to depend strongly on caustic concentration: after 4 h heat treatment at 80°C , 35% and 1% of fat were saponified with 4% and 1% NaOH, respectively (Condat-Ouillon, 1995).

Thus, it could be reasonably concluded that low surface tension in industrial NaOH solutions with $\text{COD}_s \geq 0.3 \text{ g L}^{-1}$, results from chemical reactions of NaOH with proteins and fat present in deposits from both “cold” surfaces (storage tanks, pipes operating at $\leq 50^\circ\text{C}$) and “hot” equipment (heat exchangers for preheating, pasteurising and sterilising with temperatures significantly over 50°C) regardless of the type of CIP system (single use or re-use).

3.3. Functionality of caustic soda solutions as a function of composition

3.3.1. Cleaning efficiency and membrane cleanliness

After 1 h cleaning with the four solutions studied, cleaning efficiency and membrane hydraulic cleanliness were similar (Table 3): each solution removed 91–94% of the initial membrane fouling: none of the solutions resulted in a totally clean membrane, corresponding to $R_{\text{iff(test)}} = 0$.

An efficiency lower than 0.95 has already been observed for fresh NaOH solution when cleaning a UF membrane previously fouled with skimmed milk (Daufin et al., 1991) or with a whey protein concentrate (Merin et al., 2002). Efficiency and cleanliness after cleaning with Ultrasil 13 of less than 1 could be due to the temperature used (50°C), being lower than recommended by the supplier (80°C).

Cleaning with both contaminated NaOH solutions with low surface tension showed that their content of COD_t, COD_s and SS reduced neither the efficiency nor the hydraulic cleanliness (Table 3). These results differed from those reported by Merin et al. (2002) who tested the efficiency of a re-used industrial caustic solution ($[\text{NaOH}] = 17.6 \text{ g L}^{-1}$, COD_t = 4.5 g L^{-1} , COD_s = 2.8 g L^{-1} , $\gamma = 30 \text{ mJ m}^{-2}$, SS =

790 mg kg^{-1}) when cleaning a UF membrane fouled with whey protein concentrate. The reported efficiency was around 0.88, close to that of NaOH solution contaminated with SS. But the hydraulic cleanliness was much lower (0.24) than that found in the present work (0.71), probably due to a more pronounced re-fouling of the membrane by compounds contained in the re-used NaOH solution: the qualitative composition of the latter was variable as a function of CIP and dairy equipment and was different from that of our model solution. Moreover, according to Merin et al. (2002), cleaning with microfiltrate and nanofiltrate of industrial solutions with low γ ($30\text{--}35 \text{ mJ m}^{-2}$), but with no SS, yielded an efficiency of 0.97 and 0.98 and a hydraulic cleanliness of 0.59 and 0.62, respectively, both being higher than those found with fresh NaOH: 0.95 and 0.44, respectively. Despite the variable caustic concentration during each experiment, the results showed a positive effect for γ and a negative effect for SS on cleaning efficiency and cleanliness. The negative effect of SS has already been reported regarding cleaning of stainless-steel tubes fouled with whole milk by using NaOH for 20 min at room temperature (Henck, 1993): the soil removal efficiency was 72% using fresh 2% NaOH vs. 56% and 61% by a 2% NaOH solution contaminated with 3% whole milk and by its microfiltrate (SS = 0), respectively.

It was concluded that the efficiency and hydraulic cleanliness obtained with the solutions under study were not appropriate criteria for dissociating the role of each the parameters, SS and γ .

3.3.2. Cleaning kinetics

Significantly different cleaning kinetics were measured with the four detergent solutions tested (Table 3).

With Ultrasil 13 and fresh NaOH solution, an OD peak appeared in the permeate stream after 2 min cleaning, due to the very fast removal of membrane pore fouling (Fig. 2). Afterwards, the OD signal significantly decreased to a fairly constant value after 4 min (0.07 h) with Ultrasil 13 and after 10 min (0.17 h) with fresh NaOH. Simultaneously, the retentate OD increased (results not shown) due to its enrichment with compounds extracted from the fouling layer during cleaning; then it quickly stabilised ($t < 3 \text{ min}$). From the amount of deposit removed by closed loop cleaning, calculated according to Eq. (6), the total amount of material accumulated on the membrane prior to cleaning was estimated to be less than 8 mg of DM (corresponding to 177 mg m^{-2} membrane area).

For the trials using the recycled NaOH solutions (with and without pre-clarification), the permeate OD signal was quite different. The permeate peak corresponding to the initial removal of fouling material from the membrane pores was actually not observed. This could be due to (a) the high absorbance of the initial contaminated NaOH solutions (17.4 and 11.7 for solutions with and without SS, respectively) and consequently of the retentates, which could mask the permeate peak, and/or to (b) an inadequate sampling frequency in the first minutes of the filtration.

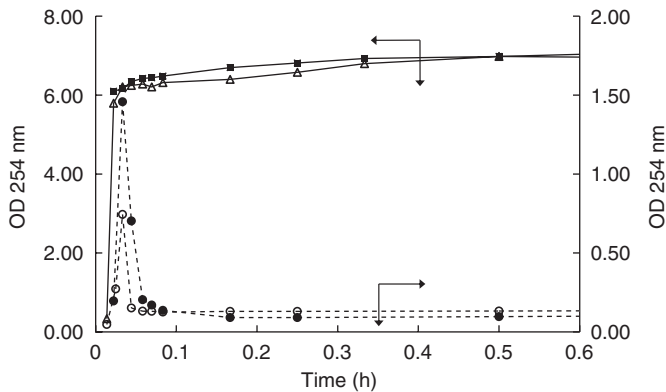


Fig. 2. Evolution of permeate optical density (OD) (254 nm) in the course of time during the alkaline cleaning of ultrafiltration membrane (initially fouled with skimmed milk) where—○: Ultrasil 13; ●: Fresh NaOH; ■: Contaminated NaOH without suspended solids; △: Contaminated NaOH with suspended solids.

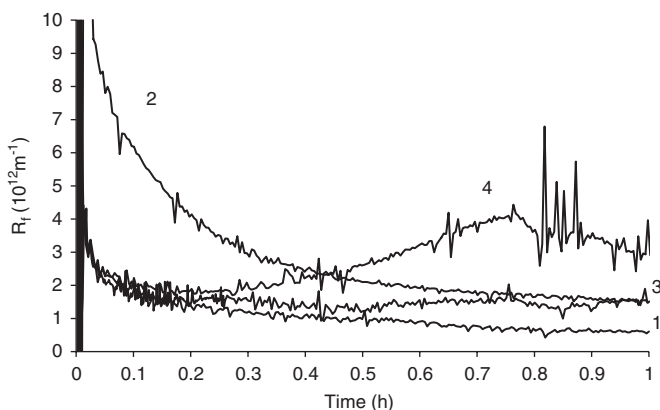


Fig. 3. Evolution of the fouling hydraulic resistance (R_f) in the course of time during the alkaline cleaning of ultrafiltration membrane (initially fouled with skimmed milk) where—1: Ultrasil 13; 2: Fresh NaOH; 3: Contaminated NaOH without suspended solids; 4: Contaminated NaOH with suspended solids.

Regardless of the detergent solution used, the hydraulic resistance of the global fouling, R_f decreased sharply during the first few minutes (Fig. 3), confirming the rapid removal of the major part of fouling as observed through the 254 nm OD signal. However, the decrease of R_f depended on the solution studied. With Ultrasil 13 and fresh NaOH, R_f decreased continuously, showing that cleaning was progressing during the whole experiment (1 h) with no indication of significant re-deposition of material extracted by the solution. Using contaminated NaOH with no SS, R_f reached a stable value after 10 min, showing that cleaning was achieved. The cleaning with the contaminated NaOH solution with SS showed the competition between foulants removal and membrane re-fouling by SS, which prevailed after 10 min cleaning, resulting in R_f increase. The R_f decrease during the first 10 min was stronger for the three solutions with low γ , in contrast to that for the fresh NaOH solution (Fig. 3). Kinetics constants (Table 3,

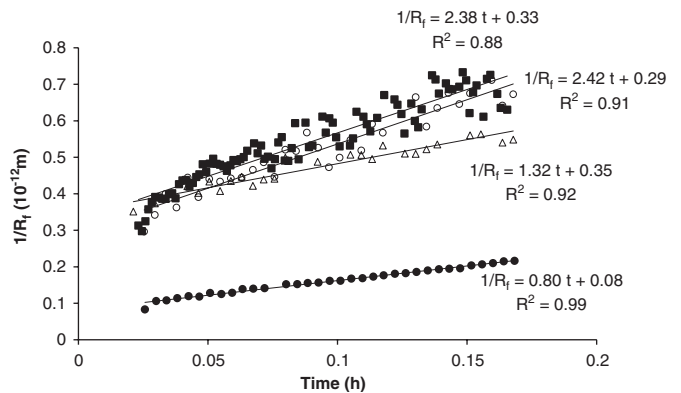


Fig. 4. Evolution of $1/R_f$ (R_f : hydraulic resistance due to the overall fouling) in the course of alkaline cleaning where—○: Ultrasil 13; ●: Fresh NaOH; ■: Contaminated NaOH without suspended solids; △: Contaminated NaOH with suspended solids (second-order kinetic model).

Fig. 4) with Ultrasil 13 and contaminated NaOH with no SS were similar ($24 \pm 2 \times 10^{-13} \text{ m h}^{-1}$), 1.8 and 3 times higher than those with NaOH with SS ($13 \pm 1 \times 10^{-13} \text{ m h}^{-1}$) and with fresh NaOH solution ($8 \pm 1 \times 10^{-13} \text{ m h}^{-1}$), respectively. Thus, the positive effect of both low surface tension and low SS content was highlighted, in agreement with the effect of a complexing agent (EDTA) and anionic surfactants which show a cleaning kinetics constant (second-order kinetics model) about twice as high as that found for fresh NaOH (Daufin et al., 1992). Thus, the two major characteristics of alkaline detergent solutions with regard to cleaning efficiency (cleanliness and especially kinetics) are pH (OH^- concentration) and surface tension.

It appears that a clarified contaminated cleaning solution with both low surface tension and $\text{SS} = 0$ operated as efficiently as a commercial detergent at the same temperature (50°C). Consequently, it is possible to advantageously replace single use complex formulations with a re-used NaOH solution having both low γ and low SS for cleaning UF membranes fouled with skimmed milk and likely with whey proteins (Daufin et al., 1991). CIP with re-used NaOH could therefore be coupled with a removal operation of SS by MF, UF or NF, which are more efficient than centrifugation (Alvarez, 2003; Dresch et al., 1999; Dresch, Daufin, & Chaufer, 2001).

For cleaning of stainless-steel equipment, it would be necessary to perform further experimental work with “cold” and “hot” equipment to validate the kinetics data concerning the effect of the SS and of surfactant compounds present in the re-used caustic solutions. The fouling of metal surfaces is different from that of membranes, due to both the nature of the particulate materials compared (solid metal vs. porous membrane) and due to the difference of temperatures used (either $4\text{--}10^\circ\text{C}$ or $>70^\circ\text{C}$ for stainless-steel equipment and around 50°C for membranes). Moreover, the experiment ought to be undertaken on an industrial scale since correctly reproducing fouling conditions (fluid

temperature, wall temperature, hydrodynamics, time) on a laboratory scale is very difficult or even impossible to achieve (Tissier et al., 1983).

4. Conclusion

The surface tension of caustic solutions used for CIP of dairy equipment decreased from the very beginning of the cleaning process simultaneously to loading charge increase (COD_t, COD_s, SS) regardless of the equipment type and the kind of CIP processing (single use or re-use). The decrease of surface tension was shown to result from the chemical reactions (alkaline hydrolysis) in the cleaning caustic solutions.

The cleaning of an UF membrane, initially fouled with skimmed milk, with re-used caustic solution having naturally lowered surface tension, showed a much faster cleaning rate compared to cleaning with fresh NaOH solution. However, the presence of SS altered this favourable kinetics constant by a factor of 1.8. Re-used NaOH solution with both low surface tension and SS could be as efficient as the single use of a commercial detergent solution.

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