Biomimetic nanostructured surfaces for antifouling in dairy processing

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Résumé :

Dans les installations de pasteurisation industrielle, l'encrassement est un problème récurrent. En effet, le chauffage du lait et de ses dérivés entraine la formation de dépôts sur les parois d'acier inoxydable des installations. Cet encrassement empêche la bonne exécution du procédé en introduisant une résistance supplémentaire au transfert thermique et menace la sécurité alimentaire en augmentant le risque de contamination microbiologique. Les coûteuses procédures de nettoyage en place, nécessaires à l'élimination régulière des dépôts, représentent des coûts financiers et environnementaux considérables. Limiter l'encrassement laitier apparait donc comme un enjeu de taille.

Les surfaces biomimétiques inspirées des feuilles de Lotus (à rugosité hiérarchisée) ou les SLIPS (Slippery Liquid Infused Porous Surfaces, inspirées des plantes carnivores Nepenthes) ont attiré l'intérêt des scientifiques, les premières pour leurs propriétés autonettoyantes, les secondes pour leurs caractéristiques antiadhésives. Ces types de surface apparaissent comme de possibles solutions au problème posé par l'encrassement laitier. Le but de ce travail est de réaliser des surfaces biomimétiques autonettoyantes et antiadhésives directement sur acier inoxydable, et de tester leurs comportements à l'encrassement en conditions industrielles.

Les différentes surfaces ont été étudiées avant et après encrassement pour (i) établir leurs propriétés de surface et (ii) évaluer l'impact de ces différentes propriétés de surfaces sur l'encrassement laitier. Plusieurs outils analytiques, comme la goniométrie, la cartographie RX en coupe transversale et la microscopie à balayage électronique ont été mis en œuvre dans cette optique.

D'excellentes performances anti-encrassantes ont été observées pour les surfaces glissantes : aucune trace d'encrassement n'a été observée sur ces dernières.

Abstract:

In dairy pasteurization equipment, fouling is an ongoing problem. Indeed, when heated, milk and its derivatives generate mineral and proteinaceous deposits on stainless steel walls. This heat-induced fouling impairs the process through the addition of an increasing thermal resistance to the system. Deposits are also a threat to food safety as they provide micro-organisms with good settlement opportunities. The cleaning procedures, which are mandatory for the frequent removal of the deposits, induce considerable financial and environmental costs. As a consequence, fouling mitigating strategies are desperately needed.

Biomimetic surfaces, e.g. Lotus-like surface (with dual-scale roughness) or SLIPS (slippery liquid infused porous surfaces, inspired from Nepenthes pitcher plant) have been recently investigated respectively for their self-cleaning or fouling-release properties. This work aims at designing Lotus-like and slippery surfaces directly on stainless steel and test them in dairy processing conditions to assess their fouling behaviors.

Characterizations were performed on the surfaces before and after fouling, in order to (i) establish clearly their surface properties (wettability, roughness…) and to (ii) investigate the impact of the different surface properties on heat-induced dairy fouling. Several analytical tools such as Goniometry, cross-section Electron Probe Micro-Analysis X-ray mappings, and Scanning Electron Microscopy were implemented to this end.

Slippery surfaces exhibited outstanding results, as no trace of fouling was found on them.

Keywords: antifouling, dairy, slippery surface, stainless steel, pasteurization

1. Introduction

Dairy processing industries are facing the ongoing problem of heat-induced fouling. Indeed, when heated, milk and its derivative generate deposits on stainless steel walls. Those deposits jeopardize the process through addition of an increasing thermal resistance to the system. Moreover, they endanger food safety by providing micro-organisms with good settlement opportunities. The frequent mandatory cleaning of those fouling layers generate excessive financial and environmental costs. As a consequence, fouling mitigation strategies are desperately needed.

Thus dairy fouling phenomena have been carefully studied and it has been demonstrated that the deposits were mainly constituted of protein and minerals. Moreover, their composition has been proven to vary with temperature, as under 100°C, there are mostly proteinaceous (around 70% in weight) whereas above this threshold, minerals were the major component [1]. Extended research on deposits build-up mechanisms also revealed that unfolded protein clusters were first to deposit onto stainless steel [2], which led to the conclusion that protein adherence to the substrate was crucial to control in dairy fouling management.

Different remediation paths have been proposed to limit protein fouling on various substrates, and a majority of them involve coating stainless steel with protein repellent [3], [4] or antiadhesive materials [5], [6], respectively leading to antifouling or fouling-release properties. Nonetheless, coating adherence to stainless steel is a major challenge to the viability of such surfaces.

Biomimetic surfaces inspired from the surface morphology of lotus leaf could be considered for their self-cleaning abilities [7]. Their dual-scale roughness (i.e. a micro-roughness superposed by nanoscale roughness) allows for the particular suspended Cassie-Baxter wetting state due to air remaining trapped between the liquid and the solid surface. Those surfaces possess very high contact angles (higher than 150°) and very low contact angle hysteresis (less than 10°). However, their stability through time remains questionable as under certain environmental conditions, liquid is very likely to penetrate into the three dimensional structures, maximizing the solid/liquid contact area and degrading the surfaces'

self-cleaning properties [8]. To overcome this limitation, impregnation of the lotus-like surfaces by a liquid of low surface tension (e.g. an inert oil, non-miscible to water) appears a possible solution. Indeed, the resulting interface would be similar to the one of SLIPS (Slippery Liquid Infused Porous Surfaces, [9], [10]), which present a smooth and inert interface that would theoretically limit fouling.

The goal of this work is in a first time to design biomimetic slippery surfaces directly on stainless steel, using laser ablation texturing to modify surface morphology and enable it to retain oil inside the dales between the micro/nano asperities. Then, antifouling performance will be assessed under industrial-like conditions using a pilot pasteurizer. Thorough characterizations, involving a wide set of analytical tools, allow understanding fouling results.

2. Material and Method

2.1. Surface modification

The surfaces tested in this work were $45*16*1$ mm^3 316L 2B stainless steel substrates (Sapim Inox, France).

Native stainless steel (called NAT hereafter, Figure 1A) was used as a reference for all testing. Prior to any test or modification, NAT coupons were degreased in a 50/50 ethanol/acetone blend and soaked for 10 minutes in a 2% (v./v.) RBS35 solution at 65°C. Rinsing was done once in 50°C deionized water and then twice in water at room temperature.

Texturing was carried out at the department of Chemical and Biological Engineering of the University of British Columbia (Canada). Cauliflower-like structures were obtained after femtosecond laser ablation under certain laser fluence and scanning speed. Details of the procedure for texturing can be found elsewhere [11]. The resulting samples will be referred to as TEX (Figure 1B).

To maximize oil retention on TEX surface, a fluorosilanization was performed by immersing TEX samples in a 10^{-3} M solution of trichloro-perfluorooctyl-silane (Sigma Aldrich) in n-hexane for 4 hours. Rinsing was done once in hexane, twice in dichloromethane and once in ethanol. The surfaces, called SilTEX in the paper, were then dried under ethanol flow.

Slippery liquid infused surfaces (called SLIPS-like in the rest of the paper) were obtained by pouring dropwise Krytox 103 oil (DuPont) on tilted SilTEX surfaces. They were left in this position to allow the excess oil to drip off.
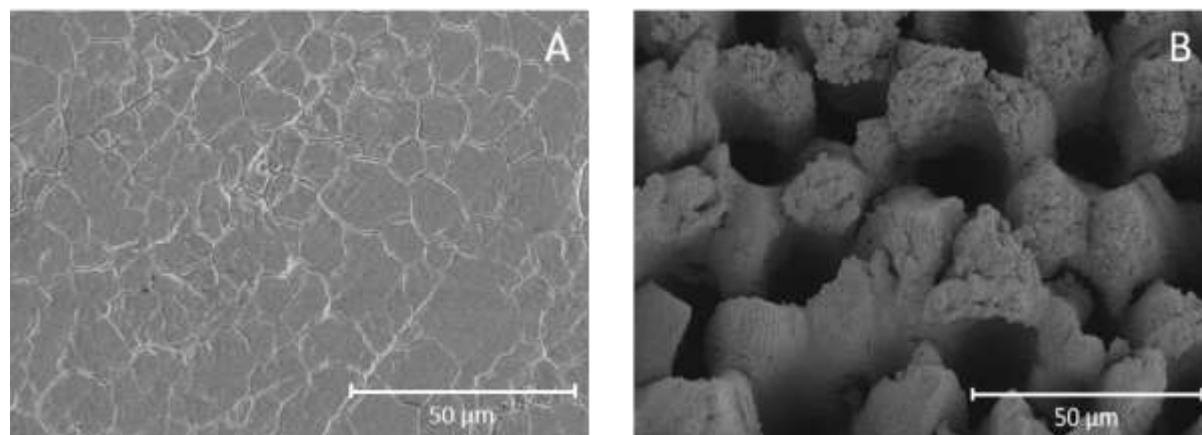

Figure 1 : SEM micrographs of native stainless steel (A) and laser textured cauliflower-like stainless steel (B).

2.2. Fouling tests

A pilot-scale pasteurizer was used to study the fouling performances of the different surfaces (Figure 2). It is composed of a storage tank connected to two plate heat exchangers in counter-current configuration, one for preheating (from 20 to 65°C) and one for heating (from 65°C to 85°C). Sample holders were placed right at the outlet of the heating section. In those tests, milk was modelled by a 1% (w./v.) whey protein powder (Promilk 852 FB1, IDI SAS, France) in reverse osmosis water. Calcium content was adjusted to 100 ppm by addition of $CaCl_2$. The model fluid flow rate was 300 l/h and was circulated for one and a half hours. Some NAT and SLIPS-like samples were then submitted to a 20 minutes rinsing step where the model fluid was replaced with hot water, to investigate potential fouling-release properties.
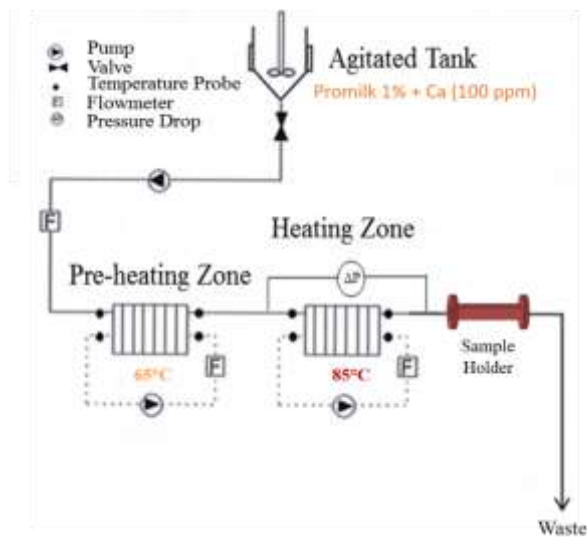

Figure 2 : Schematic representation of the pilot pasteurization facility.

2.3. Surface characterization

Goniometry

Wettability studies were carried out on a DSA100 goniometer (Krüss, Germany) equipped with a tilt table allowing dynamic analysis (contact angle hysteresis, roll-off and slide-off angles). Droplet volume was fixed to 8 μL.

Surface energy measurements (SFE) were done on a GBX goniometer. Van Oss approach was used for metallic substrate (probe fluids were deionized water, formamide and diiodomethane). This method allows the calculation of total surface energy (γ^{Total}) and of its different components: γ^{LW} due to dispersive interactions, γ^{AB} due to acido-basic interactions. γ^{AB} is further subdivided between γ^+ and γ^-, the electron acceptor and electron donor components respectively. On the other hand, Wu's method (with water and diiodomethane) was implemented for oily interface. This method allows to calculate γ^{Total}, γ^{LW} and γ^P which is the polar component of the surface free energy.
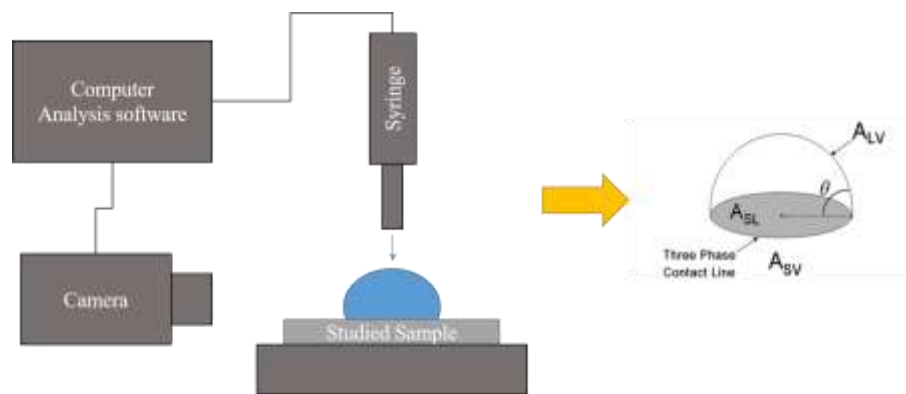
Figure 3 : Schematic representation of the goniometry measures.

Profilometer

Surface roughness was characterized with an AlfaStep IQ stylus-type profilometer (Figure 4). The cantilever travelled at 20μm/s on 500 μm segments.
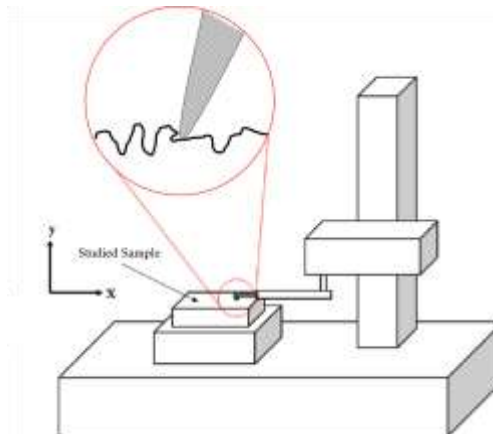

Figure 4 : Diagram of a stylus-type profilometer (adapted from [12]) .

Scanning electron Microscopy (SEM)

SEM observations were carried out on a Hitachi S4700 equipment. Acceleration voltage was 5 kV and current intensity was 15 μA.
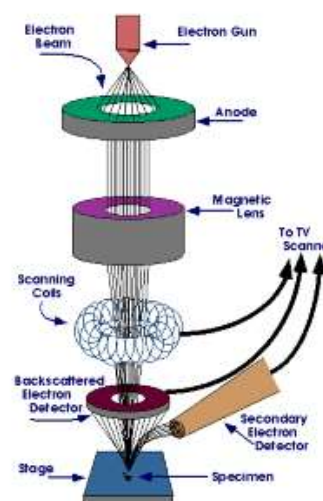

Figure 5 : Principle of Scanning Electron Microscopy [13].

Electron Probe Micro-analysis (EPMA)

A Cameca SX100 EPMA was implemented to observe fouled samples in cross-section. X-Ray mappings were carried out at 15 kV and 40 Na; Different crystals were used to detect the Kα of Sulphur (for protein) and Calcium (for mineral fouling) on the one hand, and Iron (for stainless steel substrate) on the other hand: PET and Li respectively.
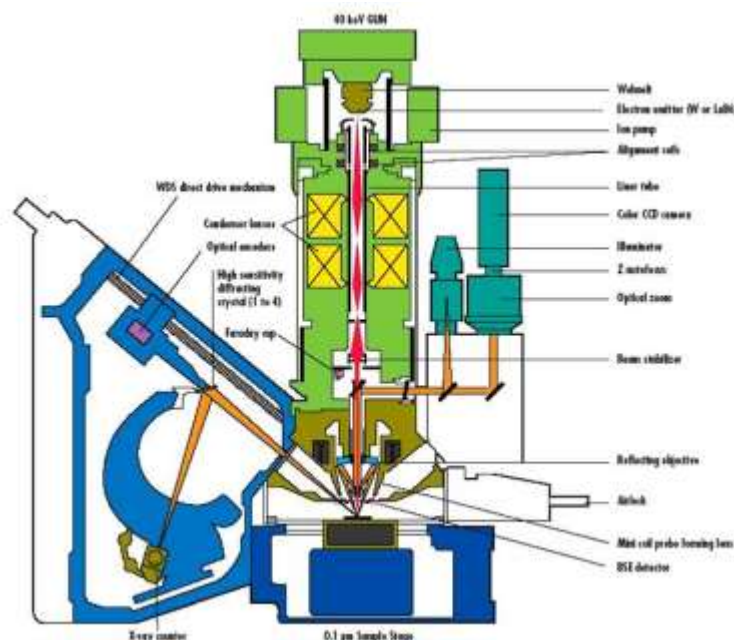

Figure 6 : Diagram of an EPMA device [13].

3. Results and discussion

3.1. Clean surface characterization

Careful pre-fouling surface characterization was necessary to fully elucidate the samples' properties. Table 1 gathers goniometry and roughness features for the different studied substrates.

Table 1: Water contact angle, surface energy and roughness of native and modified stainless steel.

	WCA (°)	γ^{Totale} (mN/m)	γ^{LW} (mN/m)	γ^{AB} (mN/m)	γ^{+} (mN/m)	γ^{-} (mN/m)	Ra (nm)
NAT	92± 5	40.5 ± 1.7	38.1 ± 0.3	2.4 ± 1.7	0.4 ± 0.3	3.5 ± 2.5	68 ± 12
TEX	0	Not possible to determine					1243 ± 18
SilTEX	133 ± 2	Not possible to determine					1364 ± 15
SLIPS-like	112 ± 1	20.3	18.9	Polar comp.: 1.4			Liquid interface

The complex roughness of TEX and SilTEX does not allow SFE to be calculated via contact angle measures, as roughness interferes with apparent contact angles, regardless of the fluid. Nevertheless, the WCA value of TEX (0°), suggests that the laser treatment significantly oxidized the surface, inducing an SFE increase compared to native stainless steel. On the other hand, the high WCA of SilTEX (133°) points out that fluorosilanization is effective to reduce SilTEX surface energy, compared to TEX. Although SilTEX did not reach superhydrophobicity (which threshold is 150°), their wetting state was investigated through dynamic goniometry and revealed a contact angle hysteresis (CAH) of 2.3° and a roll-off angle of 5°. Those wettability features are compatible with the suspended Cassie-Baxter wetting state, where air is trapped between the solid and liquid phases thus forming a composite interface. As a result, a droplet placed on such a surface rests on an air-solid composite surface and thus is very mobile.

This mobility, resulting from the small amount of solid effectively in contact with water, leads to the so-called lotus effect, which is equivalent to self-cleaning property.

Oil impregnation caused a significant decline of WCA. Indeed, in the case of liquid impregnation, the interface exposed to the environment is composed of oil (encapsulated state: a thin film of oil covers the whole surface), or of oil and solid substrate (impregnated-emerged state: some solid features emerge from the oil layer, leading to higher contact angle hysteresis due to contact line pinning on the solid surface). As air is no longer involved in the interface, the WCA is expected to decrease. Dynamic goniometry revealed an extremely low CAH of 0.6° and a slide-off angle of 2°, which allows to think that the SLIPS-like surface is in the encapsulated state, which would be the most adequate to repel dairy fouling. Oil impregnation also allows reducing surface free energy compared to native stainless steel, which is also an asset against fouling. The combination of low surface energy and slipperiness lead to expect good fouling-release properties from the SLIPS-like surfaces.

3.2. Fouling results

Weighting of samples before and after fouling allowed to determine their fouling density and to compare them to the NAT reference. Figure 7 presents the different fouling performances, F% (Equation 1).

$$F\% = \frac{M_F/_S - M_{F,ref}/_S}{M_{F,ref}/_S} * 100 \qquad\qquad \text{Equation 1}$$

Where　F%: Fouling density compared to native stainless steel (-)
　　　　M_F: Fouling mass on the sample (mg)
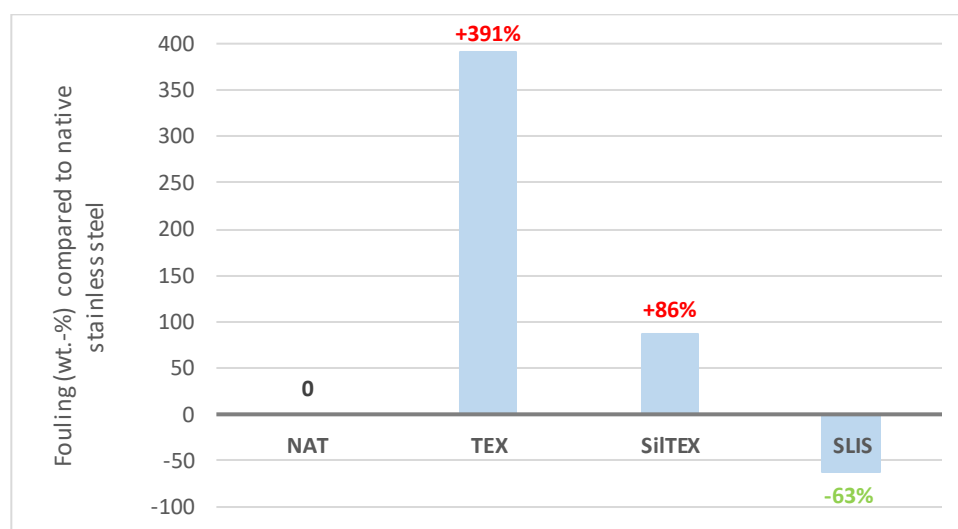　　　　S: Fouled surface (cm²)

Figure 7 : Fouling performances of different samples compared to native stainless steel.

The high surface energy and the high roughness of TEX samples appear to tremendously promote fouling growth, as an increase of 391 wt.-% of dairy deposit compared to unmodified steel is obtained. Indeed, high surface energy promotes stronger bonding of unfolded protein to the substrate, and elevated roughness is favorable to interlocking phenomenon, i.e. penetration of fouling material into surface relief (Figure 8). Interlocking stabilizes and strengthens deposit's basis and promotes further growth.

SilTEX samples do not exhibit self-cleaning properties when submitted to pasteurization; as a matter of fact, their fouling weight increases (+86 wt.-%) compared to native stainless steel. It is very likely that turbulent fluid flow triggers the wetting mode transition from suspended to impaled Cassie-Baxter state. As a result, the self-cleaning property is lost and foulant agents are able to enter the surface cavities and

dales, inducing interlocking (Figure 8). Nevertheless, comparison between TEX and SilTEX shows that surface energy reduction is efficient to mitigate dairy fouling.
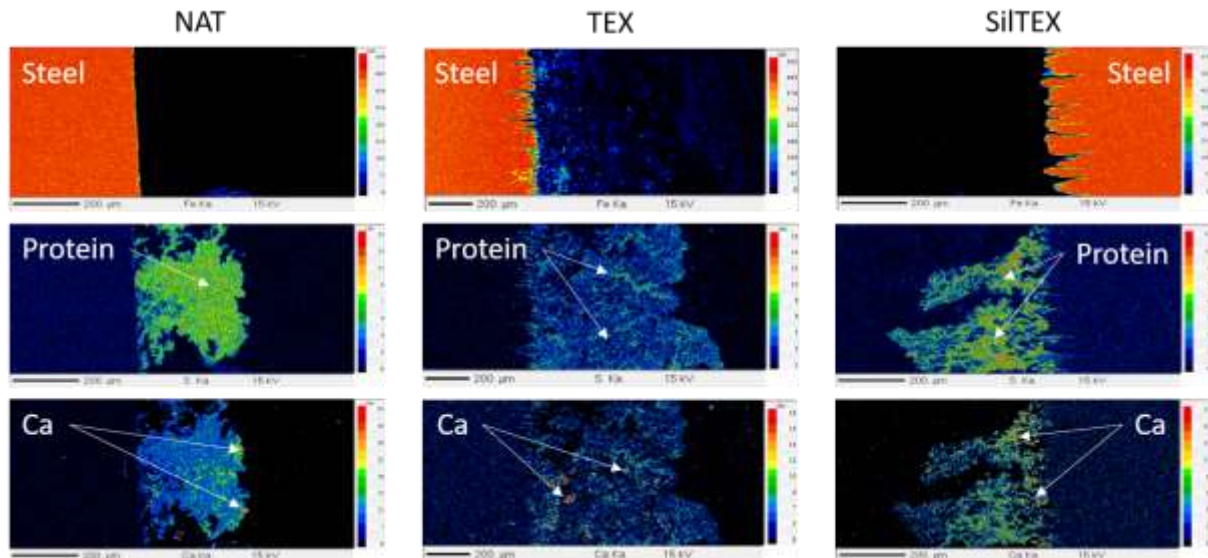

Figure 8 : Cross-section EPMA X-Ray mappings of NAT, TEX and SilTEX samples.

SLIPS-like structures lead to the most interesting results, as they allow a reduction of deposit weight by 63% compared to the control surface. This indicates that oil impregnation limits protein adhesion to the surface. Moreover, deposits on SLIPS-like look radically different from deposits on stainless steel (Figure 9). Indeed, while dairy fouling on NAT surfaces is thick and dense, the deposits on SLIPS-like samples show large bubble-like structures. This points out the very low adhesion of the deposit onto the liquid-infused substrate and suggests fouling-release properties. This was corroborated by the observation of SLIPS-like and native samples after the 20 min rinsing step, as no trace of fouling was found on liquid-infused surfaces after rinsing.
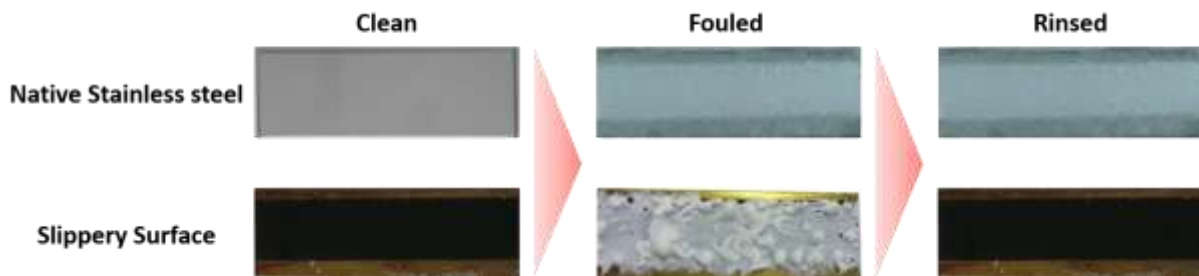

Figure 9 : Pictures of clean, fouled and rinsed native stainless steel (top) and SLIPS-like surfaces (bottom).

4. Conclusions

Lotus-like dual-scale roughness surfaces were unsuccessful to reduce dairy fouling in pasteurization conditions due to the lack of stability of the Cassie-Baxter under flow. As a result, wetting transition occurs under flow from a composite suspended Cassie-Baxter to an impaled Cassie-Baxter state, maximizing the solid/liquid contact area and thus promoting interlocking and continuous fouling build-up. On the other hand, impregnation of those surfaces with an inert, low surface tension oil, is leading to a slippery surface which was proven to be a very efficient antifouling solution, as a simple water rinsing step was sufficient to remove all trace of dairy deposit.

Acknowledgements

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