Journal of Cleaner Production 261 (2020) 121254

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Cleaning maps: A multi length-scale strategy to approach the cleaning of complex food deposits

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ARTICLE INFO

Article history:
Received 10 October 2019
Received in revised form
9 March 2020
Accepted 19 March 2020
Available online 25 March 2020

Handling editor: Baoshan Huang

Keywords:
Cleaning map
Complex deposits
Starch-fat
Cleaning-in-place
Micromanipulation

ABSTRACT

The removal of fat/starch deposit from stainless steel surfaces was investigated analysing the influence of several factors such as fat/starch proportion (0–100%), pH (3–13.2), temperature (40–50 °C), time (10–20min), surfactant (1 g/L linear alkylbenzenesulfonate) and α-amylase and lipase (0.2 g/L). To evaluate cleaning effectiveness, both a micromanipulation technique which measures cohesion and adhesion forces of deposits upon specific substrates and a device which simulates an industrial Cleaning-in-Place system, were used. "Cleaning maps" were used to visualise detergency, finding that deposits with high-starch content required alkaline solutions for reaching high detergency values (close to 85% at 50 °C). The resistance of these complex deposits to mechanical removal changed from strong adhesive and cohesive interactions to reduced cohesive forces as the starch concentration diminished. For deposits with high fat content, the highest detergency value (close to 80%) was reached at 50 °C with the chemical solutions tested, being pH = 7 the solution which could reduce the environmental impact of the cleaning process. For deposits, which showed low cohesive/adhesive forces, chemical action was not required to reach the required cleaning efficiency. The use of α-amylase or lipase (0.2 g/L) did not significantly improve cleaning, suggesting it is not recommended for either high-starch or high-fat deposits.

The multiscale "cleaning map strategy" is shown to be an effective approach to visualise the influence of Sinner factors on the cleaning of fat/starch deposits, allowing selection of the most appropriate conditions to achieve the required level of cleanliness with the lowest environmental impact.

1. Introduction

Cleaning and disinfection constitute a critical phase within food manufacturing processes, which can require approximately 20% of the total production time for food and beverage plants (Jude and Lemaire, 2013). Food deposit formation results in operational challenges such as increased pressure drop and reduction of heat transfer, impairing equipment efficiency and functionality, as well as incurring increasing operational costs (Trinh et al., 2017). Furthermore, product quality can be affected due to microbial growth or cross-contamination, causing serious hygiene problems. Cleaning-In-Place (CIP) systems are commonly implemented to obtain a consistent and reproducible cleaning efficiency, minimising the time required for dismantling equipment. These cleaning processes are well developed and automated, but nevertheless are rarely optimised (Fryer et al., 2006). Optimisation of CIP protocols can save operation time, raw materials and energy required, contributing to a more sustainable process. The reduction of the environmental impact of industrial cleaning (e.g. reduction of processing time, water consumed and chemicals) will become more important in the future, where optimisation of cleaning operations in industry becomes an unavoidable challenge (Goode et al., 2013).

The effectiveness of cleaning depends on a number of factors, such as the soiling agent, soiled surface, temperature, hydrodynamic forces, detergent formulation, and cleaning time (von Rybinski, 2007). 'Sinner's circle' describes the four major factors that need to considered in any cleaning operation: time, temperature, mechanical and chemical action (Basso et al., 2017). It suggests that the reduction of one factor can be compensated by any of the

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https://doi.org/10.1016/j.jclepro.2020.121254
0959-6526/

others three. However, a cleaning correlation is obtained empirically for each specific type of deposit, and is not easy to extrapolate to different deposit composition or cleaning conditions. A recent review of factors affecting the efficiency of clean-in-place procedures in closed processing systems is Li et al. (2019), which pays special attention to the hydrodynamic effects during cleaning.

Several types of deposits known to cause severe issues during cleaning have been studied, in particularly whey proteins (Christian and Fryer, 2006), starch (Jurado-Alameda et al., 2015) or both (Otto et al., 2016). Fats, mixtures of mono, di- and tri-glycerides, as well as other hydrophobic components are also hard to clean (Ali et al., 2015). Furthermore, these compounds can form complex deposits consisting of proteins and starches after being subjected to thermal treatment. Food deposits, thus tend to be multicomponent and micro-structured, as well as being subject to variations in morphology, topology, and electrostatic conditions across the substrate (Cuckston et al., 2019).

In addition to the cleaning parameters discussed above, an effective and comprehensive approach to optimise CIP protocols must consider the type and composition of the food deposits, and their corresponding cleaning characteristics -Laboratory methods that predict cleaning behavior are also necessary (Helbig et al., 2019). Palabiyik et al. (2015) studied the adhesive and cohesive strength of deposits, such as toothpaste, aiming to design of specific cleaning protocols. Higher temperature decreased both the deposit strength and the cleaning time, favouring diffusion through the deposit and suggesting that when molecular bonds have to be broken, chemical processes dominate (Liu et al., 2007). Surface coating and characteristics also affect cleaning; for example, Magens et al. (2017), found in the removal of sponge cake batters (made from commercial cake mix, egg powder and vegetable oil) that cake removal was very sensitivity to the oil content. These two papers examine the mechanical forces associated with the cleaning of dried deposits without chemical cleaning. More recently, Cuckston et al. (2019) studied the influence of detergent formulation on cleaning efficiency for a baked complex carbohydrate-fat food deposit adhered to stainless steel. The deposit removal increased noticeably with hydration, and was highly dependent on the cleaning solution tested. At room temperature, removal resulted from cohesive failure, while increased temperature increased the tendancy to adhesive failure. These studies only used a single type of deposit, and do not give generic design principles for CIP practice. CIP optimisation requires studying of how changes in deposit composition and/or alterations of the cleaning conditions affect the forces involved in removal, and thus the final cleanliness achieved (Piepiórka-Stepuk et al., 2016).

Fryer and Asteriadou (2009) proposed a relationship between the deposit and the type of cleaning required in a preliminary cleaning map (Fryer et al., 2011), where the most difficult deposits to clean were classified as Type 1 (highly viscous or viscoelastic fluids), Type 2 (biofilms), and Type 3 (complex solids that require cleaning chemicals). The present work aims to further develop the "cleaning maps strategy" for starch/fat deposits, identifying optimum cleaning parameters by (i) measuring the cohesive and adhesive forces of deposits, (ii) studying the total detergency achieved after CIP and (ii) application of a systematised methodology to optimise cleaning protocols. Cleaning efficiency is measured by both a micromanipulation system and a lab-simulated CIP device.

2. Materials and methods

2.1. Materials

Potato soluble starch (analytical grade, Panreac, Barcelona, Spain) and pork lard (El Pozo) were used to prepare the mixed deposits. Sudan III (Panreac, Barcelona, Spain) was used as a dye to identify the fatty fraction. Two enzymes, a thermostable α-amylase 4-a-D-glucanglucanohydrolase from *B. licheniformis* (optimal pH range of 7–9, stable between 40 and 60 °C) and a lipase from *Aspergillus oryzae* called Lipolase 100L (optimal pH range of 6.5–8.5, stable below 60 °C) were used in the cleaning formulations studied. Both enzymes were purchased from Sigma-Aldrich (A3403 and L0777, respectively). Linear alkylbenzenesulfonate (LAS), an anionic surfactant supplied by Cepsa Química (San Roque) was used as surfactant (composition in dry weight was 21.9% C13, 28.9% C12, 32.6% C11, 16.6% C10).

Cleaning tests were carried out with aqueous solutions of different pH: pH 3.0 (0.1 M citric acid and 0.2 M disodium phosphate), pH 7.0 (0.1 M monosodium - disodium phosphate buffer), and pH 13.2 (5.8 g/L NaOH; similar solution to that used during alkaline cleaning in CIP processes (Bird and Fryer, 1991).

2.2. Substrate and soiling method

Coupons of square stainless steel 316L (2.54 × 2.54 cm) at three different surface finishes (mirror 0.030 ± 0.005 μm; satin 0.309 ± 0.010 μm; and brush 0.825 ± 0.128 μm) were used as substrate to represent industrial surfaces in micromanipulation measurements. For simulated CIP tests, spherical coupons of stainless steel 410 fibers (fiber width of 0.51 mm), with an approximate diameter of 2 cm, weight between 0.80 and 0.85 g, and a free volume fraction of 93% (Jurado et al., 2015) were used as substrate for soiling. Each experiment was carried out using eight coupons.

Mixtures of fat (previously colored with Sudan III) and gelatinised starch with various fractions were used as soiling agents. The starchy component was prepared by heating a potato starch solution (30% w/w) at 68 °C with agitation for an hour (Souza and Andrade, 2002), and letting it cool at room temperature for 1 h. Pork lard was heated below 50 °C to prepare the fat fraction - fat-soluble dye Sudan III was introduced at a concentration of 0.02% w/w. The colored fat was subsequently vacuum filtered to remove the dye molecules not solubilised, and then cooled at room temperature for 1 h. Finally, the fat and the starchy fractions were mixed to specific proportions and homogenised using an Ultra-turrax (T25 digital, Ika, Spain) device for 3 min at 11000 rpm. The mixtures were left to stand at room temperature for 24 h before being used. The mixed deposits (F0 = 0% fat/100% starch; F30 = 30% fat/70% starch; F60 = 60% fat/40% starch; F80 = 80% fat/20% starch and F100 = 100% fat/0% starch) (in dry basis) were prepared to evaluate the influence of deposit composition on the cleaning process.

Table 1 shows the composition of the gelatinised starch and the lipid profile of the fat used. For the starch gel, moisture content was determined by weight loss after lyophilisation (Cryodos-80, Telstar), while protein was determined by the Kjeldahl method (conversion factor equal to 6.25) (Jiang et al., 2014). The amount of fat was determined by the Soxhlet method after acid hydrolysis, and finally, the carbohydrate content was evaluated by arithmetic difference from the rest of the components. Salts were determined by ICP-OES from the ashes, using a Perkin Elmer Optima 8300 ICP-OES Spectrometer. For the fat fraction, the lipid profile was determined by gas chromatography (Agilent series 6850A) on split mode 10:1, after conversion of the fatty acids to the corresponding methyl esters using the Christie's method (Christie, 1982).

For micromanipulation, model deposit was prepared on coupons that were exposed to the soiling agent immediately after preparation. The amount of deposit adhered to each sample was kept constant and fixed for a holder (2.5 × 2.5 × 1 cm). Soiled surfaces were then kept at room temperature for a day before

Table 1
Composition of the starch and fat fraction of the mixed deposits.

Gelatinised starch	
Composition	**Concentration**
Carbohydrates (g/100 g)	28.07
Fat (g/100 g)	0.06
Protein (g/100 g)	0.09
Water (g/100 g)	71.45
Ashes (g/100 g)	0.32
Mg (mg/100 g)	6.75
K (mg/100 g)	13.00
Ca (mg/100 g)	4.93
Na (mg/100 g)	105.15

Pork lard	
Fatty acid	**Concentration (% w/w)**
Palmitic (C16)	25.08
Palmitoleic (C16:1n9)	1.35
Estearic (C18)	8.35
Oleic (C18:1n9)	58.73
Linoleic (C18:2n6)	4.74
Asclepic (C18:1n7)	1.74
Saturated fatty acids	33.43
Monounsaturated fatty acids	61.83
Polyunsaturated fatty acids	4.74

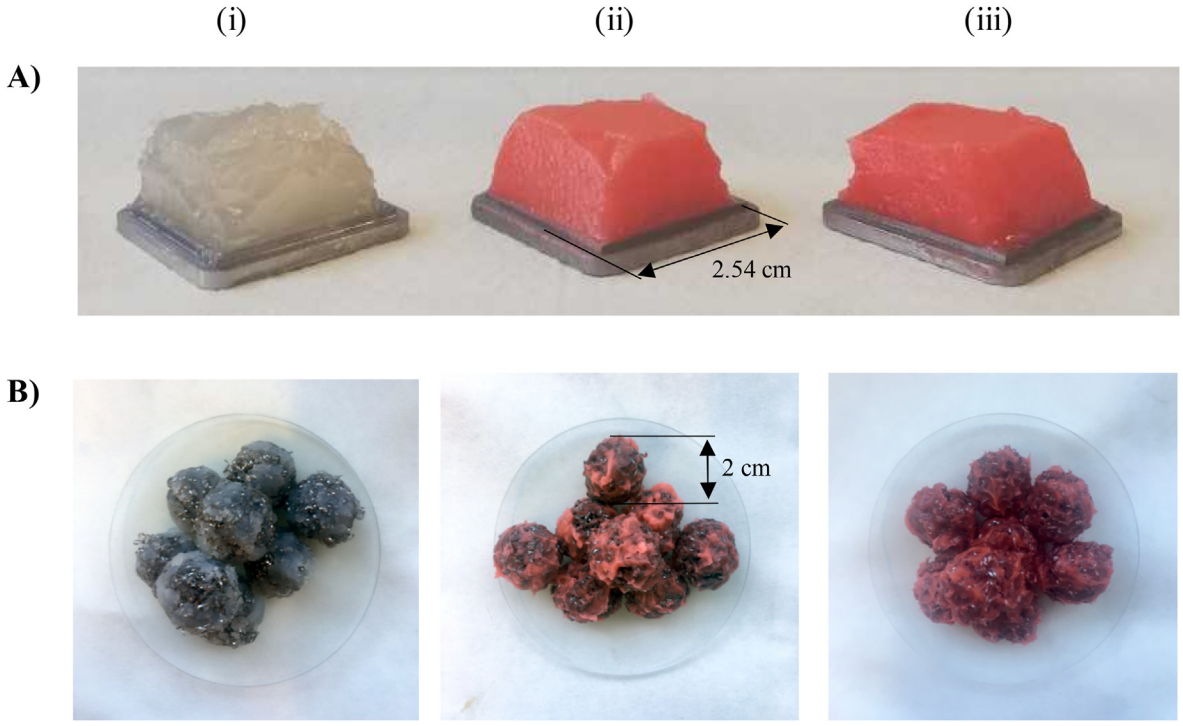

Fig. 1. Stainless steel flat (**A**) and spherical coupons (**B**) soiled with (i) gelatinised starch (F0), (ii) mixed deposit with 60% (w/w) fat on dry basis (F60) and (iii) colored pork lard (F100).

testing. For the model CIP, spherical stainless steel coupons were soiled uniformly by rolling them on a surface covered in mixed deposit. Each sphere retained 2.0 ± 0.5 g deposit, with a total mass of deposit of 16.0 ± 1.0 g in each cleaning test with 8 spheres. The soiled spheres were kept at 4 °C for 30 min before being used. Fig. 1 shows the appearance of the soiled stainless steel coupons and spheres (gelatinised starch (F0), a mixture (F60) and colored pork lard (F100)).

2.3. Mechanical removal: micromanipulation

The operational principle of the micromanipulation device for probing mechanical removal can be found in Liu et al. (2002). The device measured the force required to scrape deposit from a surface (adhesion forces) or remove a layer of deposit (cohesion forces). During each measurement, a blade travelling at 1 mm/s scraped the deposit at 3 mm from the coupon surface at room temperature with

no chemical action (defined as stage 1). In addition, for deposit F100, another run (defined as stage 2) was done at a height of 1.5 mm from the coupon (out of a total deposit height of 3 mm). The force required to remove the deposit (mN) was measured as a function of time for 60 s. The deposit behaviour was categorised as cohesive, adhesive or mixed failure. The same scraper was used for all experimental runs and tests were repeated at least four times. Surface adhesion was varied by using three different surface finishes within the standard roughness limit defined for food contact surfaces (Ra < 0.8 μm) (Frantsen and Mathiesen, 2009). Surface roughness (Ra) and its typical deviation were determined by White Light Interferometry (MicroXAM2, KLA Tencor, California, U.S.A.) from at least four locations for each sample.

Two parameters were calculated from each force profile:

- the deposit peak force (F_{max}) which was converted to the maximum shear stress (τ_{max}) dividing by the deposit contact area (A), and
- the breakage work per area (Wb) defined as:

$$Wb = \frac{1}{A} \int_{to}^{t1} F(t) \cdot dx \quad (1)$$

where F(t) was the measured force, and t_o and t_1 are the start and end times of the experiment (Magens et al., 2017).

2.4. Chemical removal: simulated CIP

Cleaning tests were carried out in a BSF device (Bath-Substrate-Flow) proposed by Jurado-Alameda et al. (2003), which reproduced a CIP (Cleaning-In-Place) system at a laboratory scale. The BSF device comprised a (i) tank (1000 mL) where the cleaning solution was stored; (ii) a peristaltic pump that drove the washing solution circulating through a closed circuit; (iii) a packed column where soiled coupons were deposited (2.5 cm in diameter; 8.5 cm in height; 50 ml of capacity); and (iv) a thermostatically controlled water-bath. This device was previously used in studies on detergent formulations for cleaning processes in the food industry (Vicaria et al., 2017), and allows modification of the variables affecting cleaning efficiency, such as type of deposit and substrate, cleaning solution, flow rate, temperature, and cleaning time.

Here, the substrate (stainless steel fibers in spherical coupons), flow rate (120 L/h) and volume of the washing solution (1.2 L) were kept constant in all experiments. Mixed deposits prepared with gelatinised starch and colored pork lard were used as soiling agents as described in section 2.2, and cleaning investigated using different solutions. The effect of pH was evaluated by carrying out cleaning tests reproducing acid (pH 3.0), neutral (pH 7.0) and alkaline (pH 13.2) cleaning. The effect of enzymes was evaluated using 0.2 g/L α-amylase and 0.2 g/L lipase solutions prepared in pH 7.0 phosphate buffer. Cleaning tests were carried out at 40 °C and 50 °C for 10 min. Finally, the effect of cleaning time in detergency was studied using a pH 7.0 phosphate buffer solution at 40 °C, lasting 15 and 20 min. After the cleaning test, the spheres were dried for 24 h at 60 °C.

The total detergency of the mixed deposit (De, %) was calculated by weighing according to Eq. (1):

$$De(\%) = \frac{m_i - m_f}{m_i} \ 100 \quad (2)$$

where m_i was the dry weight of deposit adhered to the coupons before the cleaning process and m_f was the dried weight of remaining deposit. In this calculation, humidity content was taken into account when m_i was determined: for each cleaning test two samples of 10 g of the deposit prepared were kept at 60 °C for 24 h together with the cleaned spheres, allowing the real moisture value for each experiment to be determined. This procedure was carried out with all the deposits assayed here except for the deposit composed of 100% fat (F100); in this case, a humidity value of 0.1% was used according to the supplier information. At least three repetitions were made for each cleaning test.

The fat cleaning rate in these mixed deposits was also evaluated: the remaining fatty deposit was extracted from the cleaned spheres once dried and weighted. I-octane (99%, Panreac) was used as a solvent, spraying 50 mL through coupons until no colored deposit was observed. The absorbance of the i-octane solution was measured spectrophotometrically at 500 nm (Cary 100 Bio UV−Visible, Varian). This assay was done in triplicate. Fat concentration was evaluated using a calibration line done for each deposit tested. This procedure evaluated the quantity of fat cleaned in each test ($m_{fat\ cleaned}$) as a difference between the mass of fat initially adhered to the spheres and that remaining in the cleaned ones. In each cleaning test the fat cleaning rate (FCR, %), or cleaning efficiency relative to fat was determined according to

$$FCR(\%) = \frac{m_{fat\ cleaned}}{m_i - m_f} 100 \quad (3)$$

So that FCR represents the percentage of fat cleaned with respect to the total mass of deposit removed from the coupons. Finally, an analysis of variance (ANOVA by Statgraphics Centurion XVI) followed by Fisher's Least Significant Difference test as a multiple comparison procedure were applied to the FCR results at each temperature to determine the significance of the differences found.

3. Results and discussion

Removing complex deposits from a surface involves synergistic effects of both mechanical force and the effect of chemistry (environmental factors). The influence of both are considered separately before a combined "cleaning map", was implemented to optimise the cleaning protocol as a function of the deposit base composition.

3.1. Micro-mechanical removal of complex food deposits

3.1.1. Study of deposit mechanical behaviour

The overall force required to remove a deposit from the supporting substrate was a function of both interfacial adhesion and the cohesion of the deposit. Micro-mechanical removal was carried out to study how deposits composition affected the cleaning efficiency.

Mechanical removal by micromanipulation presented distinctive characteristics related to the deposit composition. Fig. 2 shows representative results for the deposits tested. No resistance was observed whilst the blade was approaching the foulant such as point (a) in the figure. However, force increased when initial contact was made (point b) due to the energy needed to overcome the cohesive characteristics of the foulant.

Fig. 3A and B shows typical force-time curves for removal. The maximum value recorded (F_{max} at point (c)) corresponded to the maximum force applied to remove the deposit completely, which depended on the nature of the foulant. Pure starch sample showed a mixture of cohesive and adhesive failure (Fig. 2), and a high force (F_{max} = 1170 ± 210 mN) was required to remove F0. Fig. 2A schematically shows the behaviour imaged in Fig. 2B, which shows the surface of the metal coupon after scraping: initially, cohesive breakage occurred, with deposit fracturing to leave material (i) on the surface; the peak force is then reached at point (c), which is

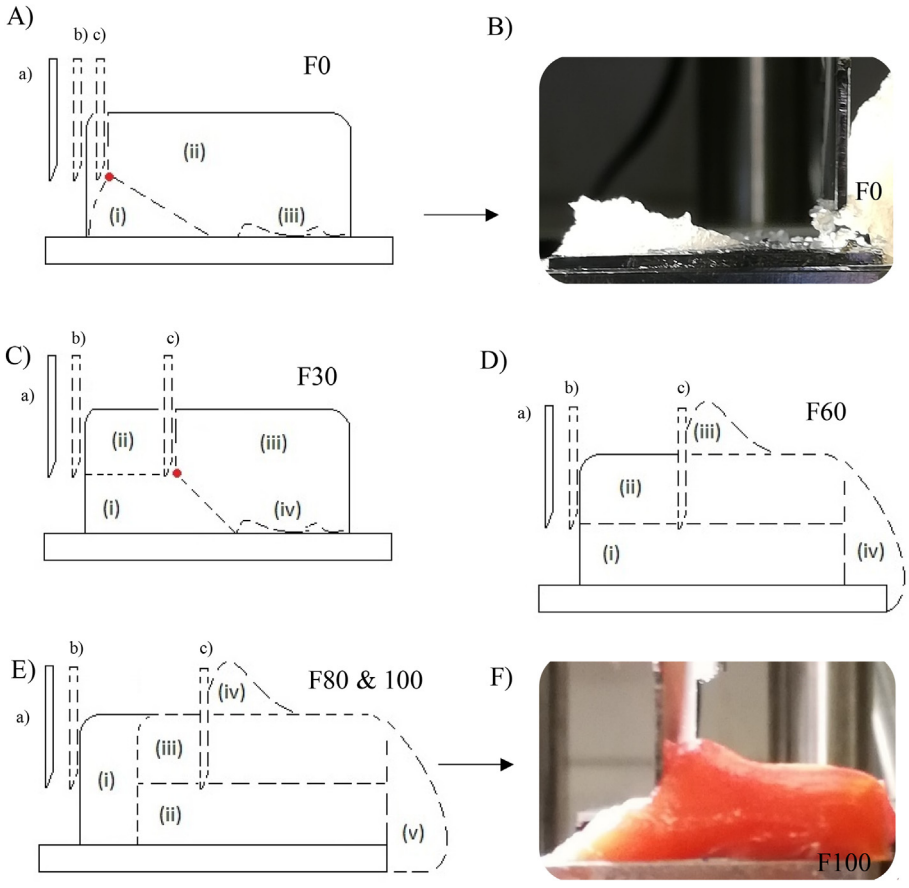

Fig. 2. Schematic mechanical behavior for each type of deposit depending on its base composition. Blade position during the mechanical removal: points of interest represented by a) b) and c).

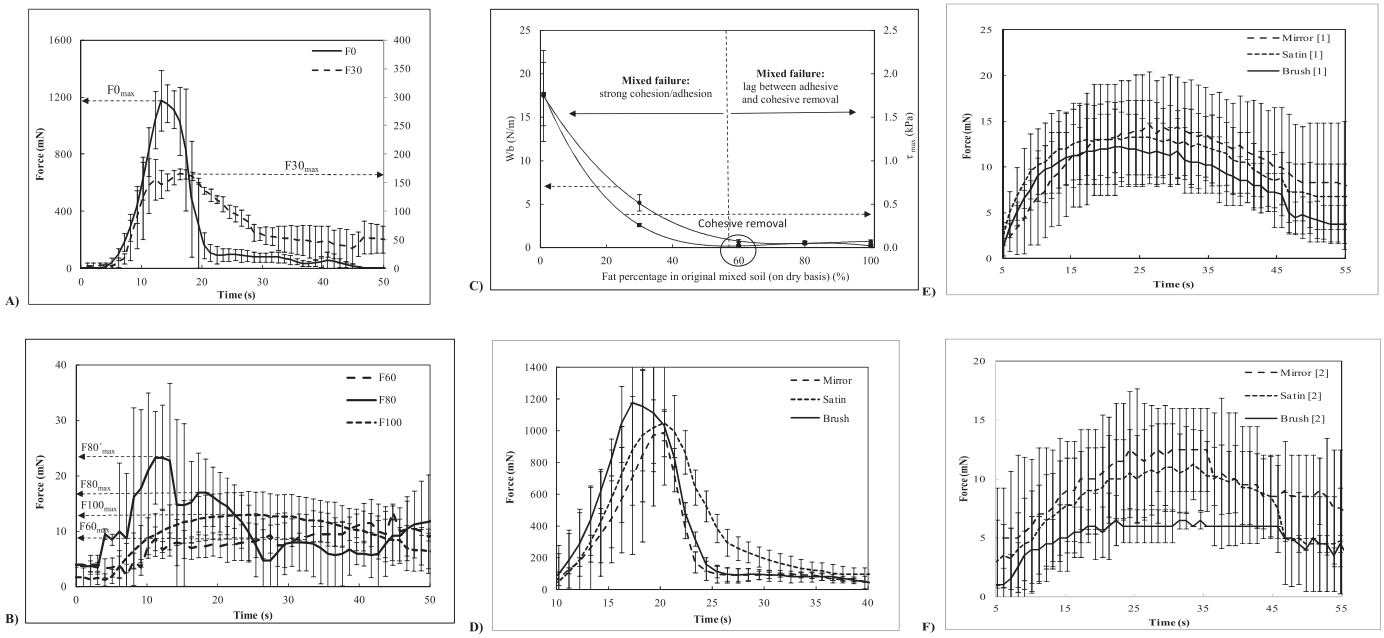

Fig. 3. Study of the mechanical removal of fat/starch deposits: A) Force curves for high-starch deposits, B) Forces curves for high-fat deposits, C) breakage work (Wb) and maximum shear stress (τ_{max}) for deposit removal depending on the fat content. Force curves upon mirror, satin and brush stainless steel 316L surfaces: F0 deposit (D) and F100 (E and F). Figure E) shows the stage [1] of scraping at 3 mm upon the coupon (7 mm of deposit over this level) and Figure F) shows the stage [2] of scraping at 1.5 mm upon the surface (1.5 mm of deposit over this level). Error bars represent ±SD of at least four repeats.

followed by adhesive failure with the removal of material (ii). Some remaining material could still be seen (iii) after the end of the test.

For F30, a substantial reduction of the maximum force was observed ($F30_{max} = 166 \pm 9$ mN, Fig. 3A). Wb values of 17.5 ± 5.2 N/m (F0) and 5.2 ± 0.9 N/m (F30) (Fig. 3C), respectively) were observed at point (c), followed by transition to adhesive failure (Fig. 2C). The deposit still showed both cohesive and adhesive behaviour, but its response to external mechanical force was different to pure starch. On contact between the blade and deposit, uniform cohesive failure of deposit in the test direction was observed until the maximum force was reached (Fig. 3A; F30max = 166 ± 9 mN). Cohesive failure then occurred (zones (i) and (ii) in Fig. 2C), followed by adhesive failure similar to F0 deposit. Most deposit was removed from the supporting substrate, with only small parts remaining (iv).

Samples with high starch fractions (F0 and F30) showed high adhesive forces at the initial stage of mechanical removal, followed by mixed failure of the deposit – both cohesive and adhesive interactions were competing for the deposit removal. The introduction of fat decreased the cohesive and adhesive interactions of the deposit, favoring mechanical removal.

For samples with high fat fractions, including F60, F80, and F100, forces for removal diminished when fat concentration increased. -Fig. 3B shows peak forces of 8 ± 3, 17 ± 5 and 12±4 mN respectively. Such reduction demonstrated the reduction of the mechanical integrity of the deposit, which enhanced the cleaning efficiency. However, a thin layer of foulant remained if interfacial adhesion was strong. This was supported by the observation that the force measured did not reduce to zero after the removal of sample F30, which was attributed to the presence of remaining deposit on the substrate.

The mechanical characteristics of deposits with high fraction of fat were consistent. In Fig. 2D, for F60, cohesive removal was seen throughout, with displacement of layer (ii) to form layers (iii) and (iv). For F80 and F100, adhesive failure occurred first, displacing the whole deposit, forming layer (i). When the deposit was trapped, cohesive failure occurs, leaving a shape seen in Fig. 2F. The initial sliding was more pronounced for F80 than F100. Due to the gap formed at the beginning of the run (i), force curves showed values related to the dragging of deposit (F80'max). Lumps of mixed deposits generated more scattered data in the final stage of the experimental runs than pure ones – pure fat deposit showed a soft and uniform layer removal (Fig. 3B). There were no significant differences between the values of maximum forces for high-fat deposits.

Finally, two parameters, the maximum shear stress (τ_{max}) and the breakage work (Wb) per area (defined in section 2.3) are plotted in Fig. 3C for each deposit type. Both parameters followed similar trend once fat was introduced. Two well-defined zones can be identified: a zone for deposits with high-starch content that showed strong cohesive and adhesive behaviour (F0 and F30 zones), and another zone for deposits rich in fat with reduced adhesive and cohesive forces (F60 to F100 zones). The deposit F60, which showed only cohesive removal, marked the change between both zones. This graph is relevant to cleaning optimisation – a change of the composition could modify the general cleaning protocol established for a processing line.

3.1.2. Controlling the interfacial adhesion force

As interfacial adhesion of the deposit contributed to the overall force required, three different surface finishes (mirror 0.030 ± 0.005 μm; satin 0.309 ± 0.010 μm; and brush 0.825 ± 0.128 μm; see section 2.3) were used for understanding the importance of surface finishing to the deposit adhesion. Force curves for deposit F0 (Fig. 3D) and F100 (Figure E and F) on mirror, satin and brush surfaces are shown. For F0 (Fig. 3D), the slope of each curve until reaching the maximum force applied, as well as F_{max}, is affected by the increased surface roughness, showing an effect of roughness on deposit removal. For F100 (Fig. 3E and F), two runs at different scraping levels (stage 1 and 2; defined in section 2.3) were done to identify the influence of roughness influence. There was a decreased removal force for rougher surfaces. This reduction was because the cohesive removal was easier for rougher surfaces, where roughness increases the force needed to drag the deposit over the metal surface. Therefore, independently of the deposit nature, a mirror surface finishing could lead to more effective cleaning. ANOVA analysis was applied to F_{max} results. The ANOVA test showed no statistical differences for both F0 and F100 as a function of surface roughness (p-value of 0.54 and 0.76, respectively), however, for F100, as closer as the scraping level is to the metal surface, the roughness differences are more noticeable (p-value of 0.24; stage 2).

3.2. Hydrodynamic removal of complex food deposits (CIP)

Sinner's circle describes the four major factors that need to considered in any cleaning operation: time, temperature, mechanical action, and chemical action (Basso et al., 2017). This section analyses alterations of the Sinner's factors as a function of the deposit composition, which has been previously related to the micro-mechanical removal forces (detailed in section 3.1).

3.2.1. Effect of pH, temperature, time and surfactant on the total detergency (De) and fat cleaning rate (FCR)

To establish the influence of the cleaning conditions (acid, neutral, and alkaline) on the removal of mixed fat-starch deposits, cleaning tests on a simulated CIP system were carried out at 40 °C and 50 °C. Total detergency results (De, %) are shown in Table 2 and Fig. 4. Significant differences were observed with temperatures. At 40 °C, De with phosphate buffer pH 7.0 was clearly lower than that obtained with acid and alkaline solutions. However, at 50 °C, solutions with pH 3.0 and 7.0 showed practically identical behaviour for all mixtures except for F100 – lower detergency for acid treatment. For deposits with high-starch content (F0 and F30 mixtures), alkaline cleaning (pH 13.2) was much more effective, reaching detergency levels greater than 80% at 50 °C. On the other hand, the composition of the cleaning solution was not significant for mixtures with high-fat content, as practically identical results were obtained with all solutions tested for F60 and F80 mixtures.

To determine if there was a preferential cleaning of fat or starch in the conditions assayed, fat cleaning rate (FCR) and total detergency (De) were analysed. Fig. 4 also compares the FCR and total detergency obtained at 40 and 50 °C with the three types of chemical treatment: acid (pH = 3), neutral (pH = 7) or alkaline (pH = 13.2) solution. This information could improve cleaning strategies, allowing increased removal of each fraction of mixed deposits. Different characteristics of the FCR could be found as a function of the cleaning conditions. Note that FCR value was 0 and 100% for F0 and F100 deposits respectively, due to the composition of the deposit. For starchy deposits (F0), neither acid nor neutral solutions could facilitate the desired cleaning, whilst high De values (82.4 ± 3.6%) was obtained at 50 °C using alkaline solution. For deposits with high-starch content (F30), De value was low for acid and neutral treatments at 40 and 50 °C (Fig. 4), while FCR was favoured especially at pH = 7. This suggests that the cleaning process was more effective in removing fat fraction. Therefore, the alkaline solution (pH 13.2), commonly used for the cleaning of starchy deposits (Nor Nadiha et al., 2010), also increased detergency of the mixed deposit, with values of 86.5 ± 1.6%, while FCR was low.

For the F60 deposits, at 40 °C, the FCR values reached after the

Table 2
Detergency of fat/starch deposits in a BSF device. Cleaning time 10 min, flow rate 120 L/h (error represent ±SD of at least 3 measurements).

T (°C)	pH	Enzyme	De (%)				
			F0	F30	F60	F80	F100
40	3.0	Without	1.2 ± 0.8	9.2 ± 1.5	40.8 ± 2.3	52.6 ± 1.9	65.0 ± 2.3
	7.0	Without	2.8 ± 1.7	1.7 ± 0.7	17.7 ± 1.3	25.8 ± 9.5	49.4 ± 2.2
		0.2 g/L α-amylase	3.3 ± 1.1	7.4 ± 2.5	23.6 ± 1.8	9.5 ± 3.9	45.3 ± 1.2
		0.2 g/L lipase	2.4 ± 0.1	8.8 ± 2.3	30.6 ± 3.0	13.8 ± 3.6	53.4 ± 4.7
	13.2	Without	51.1 ± 1.8	59.1 ± 2.5	45.2 ± 1.9	58.7 ± 0.9	81.8 ± 0.6
50	3.0	Without	9.51 ± 0.04	13.7 ± 1.4	54.2 ± 0.8	64.6 ± 1.7	62.5 ± 6.0
	7.0	Without	5.5 ± 3.2	13.4 ± 1.7	58.6 ± 4.9	64.4 ± 2.6	82.5 ± 0.8
		0.2 g/L α-amylase	16.1 ± 0.7	16.8 ± 0.4	57.2 ± 2.9	65.3 ± 1.5	82.7 ± 3.3
		0.2 g/L lipase	9.2 ± 4.6	11.3 ± 4.0	56.4 ± 2.9	64.2 ± 2.1	77.8 ± 2.4
	13.2	Without	82.4 ± 3.6	86.5 ± 1.6	54.8 ± 2.5	69.2 ± 0.9	91.2 ± 0.6

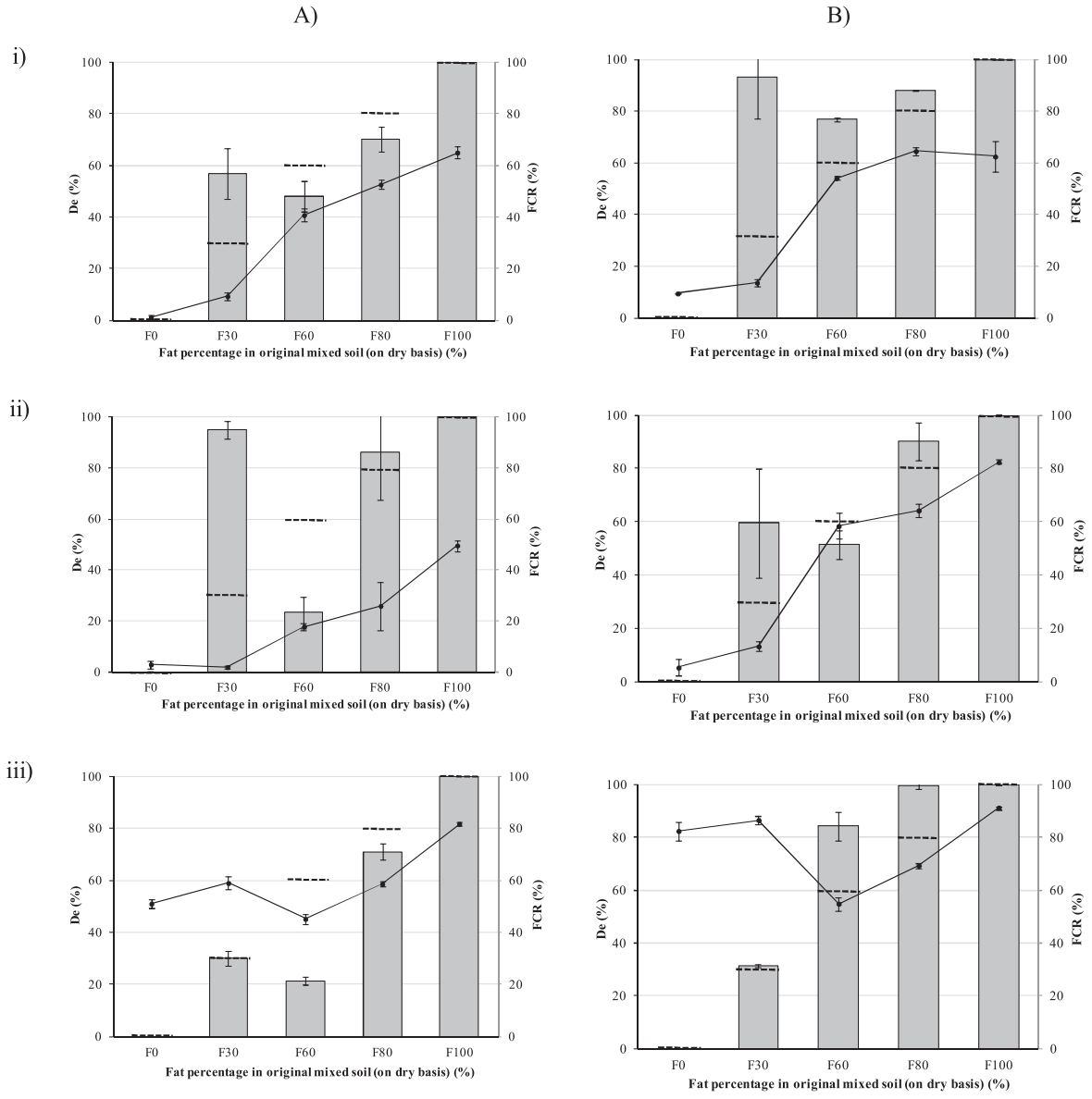

Fig. 4. In Figures 4, "a)", "b)" and "c)" should be removed from the bottom of the figures. Thank you Influence of pH on the cleaning of fat/starch mixtures. Cleaning maps of De and FCR at 40 °C (column A) and 50 °C (column B) pH: 3.0 (i), 7.0 (ii) and 13.2 (iii). Solid line = De values, dashed segments = fat rate in the original mixed deposit; bars = FCR values. Cleaning time 10 min, flow rate 120 L/h (error bars represent ±SD of at least 3 measurements).

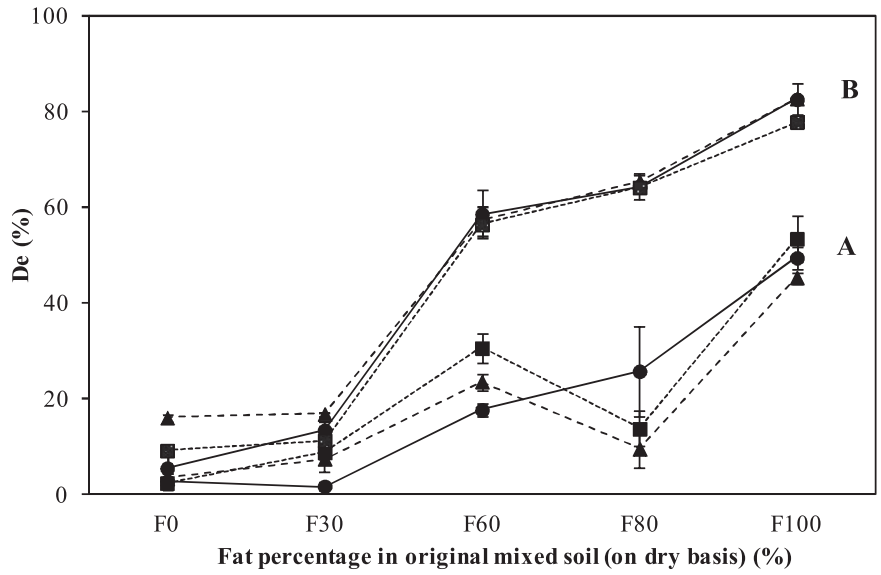

Fig. 5. Influence of enzyme addition on the detergency of fat/starch mixtures. Cleaning maps at 40 °C (A) and 50 °C (B). ● without enzyme, ▲ 0.2 g/L α-amylase, ■ 0.2 g/L lipase. pH 7.0, cleaning time 10 min, flow rate 120 L/h (error bars represent ±SD of at least 3 measurements).

cleaning assays were lower than for the original fat fraction of the deposit (Fig. 4A), suggesting that less fat was removed compared to the starchy fraction, regardless of the pH. Similar De values were observed at alkaline and acid pH, so any of the two cleaning conditions is preferable to cleaning at neutral pH. When pH = 13.2 was used, the cleaning of the starch fraction was significant, with FCR lower than for pH = 3. For cleaning assays at 50 °C (Fig. 4B), cleanability was higher than at 40 °C, regardless of the pH. In addition, analysing FCR at 50 °C, the use of acidic and alkaline solutions gave similar FCR values, higher than that for neutral conditions.

For deposits with high-fat content (F80), the use of alkaline and acid cleaning solutions was also preferable for this deposit type. At 50 °C, De values were similar independently of the solution used (Fig. 4B). The analysis of FCR shows that fat was removed in higher proportion, enhancing removal by increased temperature. This increased FCR could be related to the fact that, at this temperature, fat melted, favouring removal by mechanical action. For high-fat deposit (**F100**), higher De levels were obtained at 50 °C (Fig. 4B), the highest value for cleaning with alkaline solution (91.2%).

Taking as a reference the deposit F60 - the one that marked the zone division in section 3.1, further cleaning tests were carried out at 40 °C and pH 7.0, by (i) increasing of the cleaning time (up to 20 min) and (ii) analysing the influence of a surfactant, LAS (1 g/L), in the cleaning performance. There was no significant improvement in total detergency (De) with increased time (data not shown). In contrast, after exposing the deposit (F60) to cleaning with surfactant, FCR removal increased from 23.3 ± 6.1% to 59.3 ± 1.0%. In addition, De also increased from 17.7 ± 1.3% to 40.8 ± 1.0%. It is clear that the addition of surfactants as LAS into the cleaning formulation promoted the cleaning efficiency in removal of deposits (Chutrakul et al., 2019).

3.2.2. *Effect of enzymatic cleaning on the total detergency (De) and fat cleaning rate (FCR)*

Cleaning formulations may often contain enzymes to enhance cleaning, decreasing the energy and chemicals consumed (Gupta et al., 2003). For example, α-amylase hydrolyses starchy deposits forming water-soluble products. Here, enzymatic cleaning tests, using a pH 7.0 phosphate buffer as cleaning solution, were carried out at 40 °C and 50 °C to evaluate the influence of enzyme addition (0.2 g/L of α-amylase and lipase) on both the final detergency (Table 2) and FCR achieved.

At 40 °C, addition of enzymes increased detergency for F30 and F60 deposits (Fig. 5, lines A). Lipase enhanced the removal more than amylase for F60. However, surprisingly, the addition of both enzymes reduced the detergency of the F80 deposit. When cleaning assays were done at 50 °C (Fig. 5, lines B), increased detergency was observed for all the deposits tested with respect 40 °C, achieving similar detergency profiles (with and without enzymes) - the only enhancing of detergency was shown for F0 using amylase.

FCR values in the absence and presence of enzymes are shown in Fig. 6. ANOVA analysis was applied to the FCR results to determine differences between the cleaning conditions assayed (detailed in section 2.4). The ANOVA test showed significant statistical differences for both temperatures, 40 and 50 °C (p-value of 0.0002 and 0.0000, respectively). At 40 °C, there was almost complete removal of the fat fraction for F30, regardless of enzyme incorporation (Fig. 6A). However, increased temperature (Fig. 6B) reduced the total FCR removed. For F60 mixed deposit, the addition of enzyme produced a significant effect on removal, especially at 40 °C - lipase greatly increases the percentage of the fat removed comparing to the starch fraction. At increased temperature (50 °C), the incorporation of enzymes decreased FCR. For F80, fat removal was affected in similar way by both enzymes addition and temperature. Overall, under the experimental conditions studied, the addition of both enzymes into the cleaning solution did not significantly increase deposit removal at those temperatures, showing only FCR improvements for F30 and F60, at 40 °C, using amylase and lipase, respectively.

3.3. *Cleaning map strategy: a multiscale approach*

A systematic cleaning protocol for different mixed fat/starch deposits has been evaluated. Both mechanical and hydrodynamic removal of those complex food deposits, from micro to macroscale,

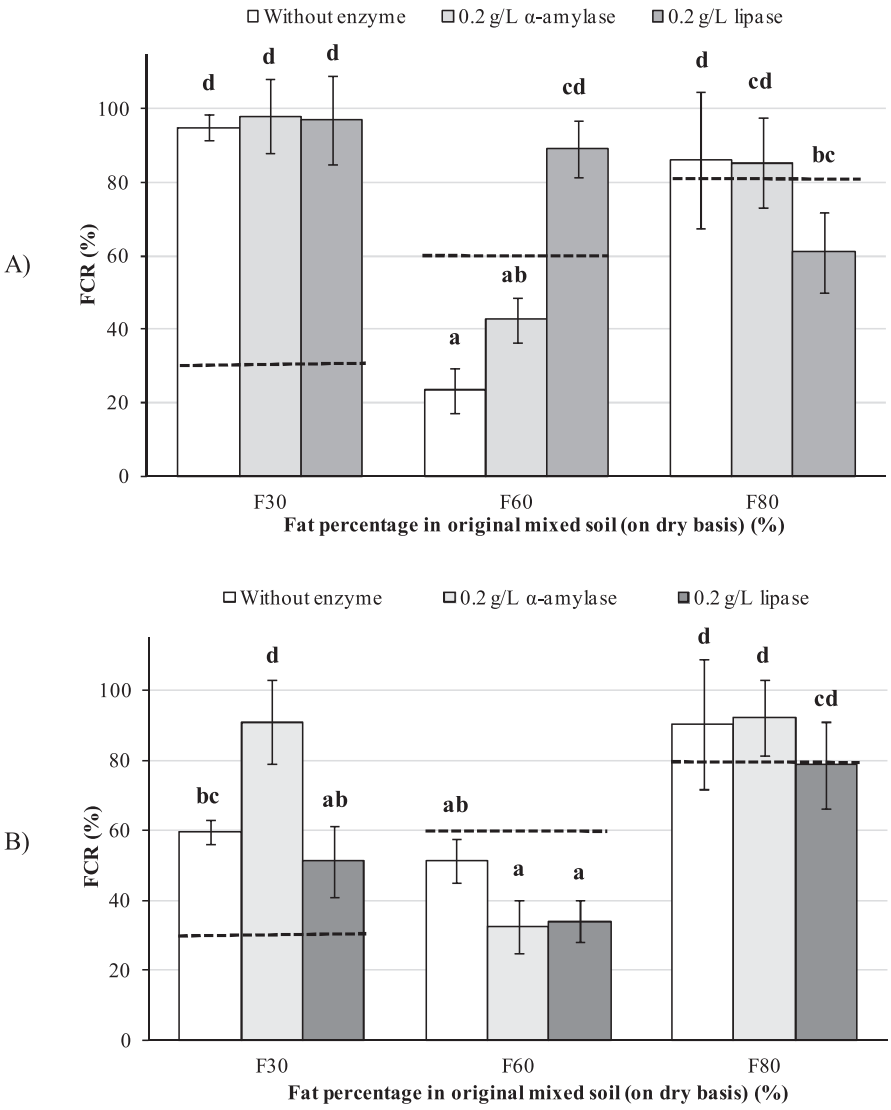

Fig. 6. Influence of enzyme addition on the FCR of fat/starch mixtures. Cleaning maps at 40 °C (A) and 50 °C (B). Dashed segments = fat rate in the original mixed deposit; bars = FCR values. pH = 7, cleaning time 10 min, flow rate 120 L/h (error bars represent ±SD of at least 3 measurements). Different letters denote statistical differences between the experimental conditions using the Fisher's Least Significant Difference test with a 95.0% confidence level.

showed a relationship between cleaning efficiency and the deposit composition. Therefore, a "cleaning map strategy" to relate both cleaning approaches has been developed for CIP optimisation.

Fryer and Asteriadou (2009) defined three types of deposits as the most difficult to clean. In this work, the two "pure" deposits, F0 (100% starch) and F100 (100% lard), were type 3 and 1 deposits respectively, and fat composition was varied from 0 to 100%. Section 3.1 showed that as fat fraction increased, resistance of the deposits towards mechanical removal shifted from strong adhesive and cohesive interactions to reduced cohesive forces. According to section 3.2, the total detergency obtained was mainly related to deposit composition, pH, surfactant and temperature. The influence of pH on removal was dependent on the fat/starch fractions. However, over the experimental range tested, no significant improvements were found when cleaning time was increased up to 20 min.

Cleaning conditions should be modified to reflect the deposit nature to achieve optimised cleaning performance, Fig. 7 shows the cleaning map developed to relate both intensity of mechanical removal and recommended cleaning conditions as a function of deposit composition. The mechanical forces needed for removal showed two well-defined zones: (i) zone A with deposits of low cohesive and adhesive interactions (fat-rich deposits), and (ii) zone B for deposits with stronger forces (rich-starch deposits). When the fat proportion was higher than the starch one, there was a significant reduction of cohesive forces, enhancing removal, while the rest remained adhered to the substrate; adhesion forces were greater than cohesive ones. When complex deposits showed strong removal forces, according to section 3.2, both chemical concentration and temperature were critical - consistent with the cleaning of deposit type 3. Alkali solution was needed for starchy deposits - sodium hydroxide, as well as other alkalis, induces depolymerisation of starch, especially when heat was applied (Lai et al., 2004). In contrast, for fatty deposits, increased temperature could melt fat at the deposit-surface interface, making it easier to dragging of the whole deposit in adhesive removal by reduction of interfacial

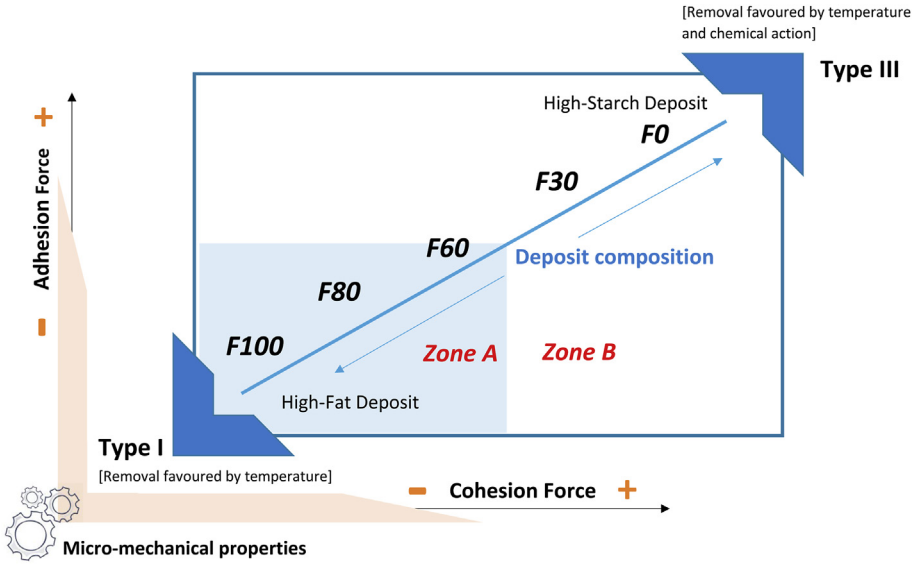

Fig. 7. Cleaning map. Micro-mechanical approach for the deposits removal as a function of their fat fraction (%) and the recommended cleaning conditions. In the graph are defined deposit type 1 and 3 as zones of specific adhesive/cohesive interactions.

forces. Removal of those deposits by pH = 7.0 solution was enhanced by temperature. These findings are consistent with the work of Goode and et al. (2013), reporting that the action of temperature could help to reduce the amount of chemicals used. Finally, as removal of starchy deposits depended on the cleaning formulation, the effect that addition of surfactant and enzymes could have on cleaning was studied. The incorporation of a surfactant such as LAS, increased the detergency under certain conditions due to the solubilisation of fat in the aqueous solution. However, addition of enzymes, lipase and α-amylase, did not improve removal significantly. The access of both enzymes could be limited for the interfaces formed by the starchy and fatty fractions.

Overall, while Micromanipulation measured cohesive and adhesive forces, CIP cleaning involved control of both interactions to enhance deposit removal. Alteration of the deposit composition affects its mechanical properties, other Sinner's factors such as temperature, chemical action, or time, should be modified accordingly. For that, the use of "cleaning maps" suggests a way of visualizing how cleaning can be affected by variations of deposit nature, allowing the required degree of detergency with reduced costs.

4. Conclusions

The removal of fat/starch deposits from stainless steel surfaces showed a clear relationship between cleaning efficiency and deposit composition. Results showed that deposit properties were critical for the selection of cleaning conditions. An attempt was made to display the results as a cleaning map, which showed that for the cleaning of **deposits with high-starch content** (F0—F30) it was necessary to use alkaline solutions, reaching high detergency values (close to 60 and 85%) at 40 and 50 °C, respectively. On the other hand, for **deposits with high-fat content** (F60 to F100), the highest detergency values (from 60 to 80%) were reached at 50 °C with cleaning solution of pH = 7 which had the lowest environmental impact due to its neutrality. Therefore, for these type of deposits, the use of acidic or alkaline solutions was not recommended because, they generate more dangerous wastewater which needs to be neutralized, with higher process and reagent costs and a greater environmental impact. The addition of α-amylase or lipase (0.2 g/L) in the cleaning formulation did not improve cleaning, so its use was not recommended for both high-starch or high-fat deposits.

Due to the chemical complexity of the deposits used and the difficulty of correlation between variables that affect cleaning process, the incorporation of "cleaning maps" in the selection of cleaning conditions enabled a satisfactory visualisation of how cleaning could be significantly affected by the composition of the deposit. This allows the most appropriate conditions to be chosen to reach a level of cleaning under conditions that are environmentally more suitable.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Otilia Herrera-Márquez: Methodology, Formal analysis, Investigation, Writing - original draft. **Mireya Serrano-Haro:** Methodology, Formal analysis, Investigation, Writing - original draft. **José M. Vicaria:** Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Encarnación Jurado:** Conceptualization, Supervision, Project administration, Funding acquisition. **Aylin R. Fraatz-Leál:** Formal analysis, Investigation. **Zhenyu Jason Zhang:** Validation, Writing - review & editing, Visualization, Supervision, Funding acquisition. **Peter J. Fryer:** Validation, Writing - original draft, Writing - review & editing, Visualization. **Alejandro Avila-Sierra:** Conceptualization, Methodology, Validation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Funding acquisition.

Acknowledgements

This work was financed by Ministerio de Economía y Competitividad, Spain (Research Project CTQ2015-69658-R). We also thank to University of Granada, Regional Government of Andalusia

and European Social Fund for the financing of contracts for technicians who have worked in this research.

The research team from Birmingham thanks EPSRC (through grant for EP/K011820), University of Birmingham, British Spanish Society, and Plastic Energy for financial support [Alejandro Avila-Sierra: BSS-Plastic Energy Award 2019].

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