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Peanut butter adsorption onto surfaces and surfactant selection in cleaning and the effect on allergen recovery

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ABSTRACT

Stainless steel and High-Density Polyethylene (HDPE) were fouled with suspensions of peanut butter and tested for their cleanability using cleaning solutions containing different surfactants. Following cleaning, protein allergen recovery from the surfaces was determined. The stainless steel was less rough (S_a = 162 nm) and less hydrophobic (-4.5 mJ/m^2) than the HDPE surface (S_a = 3261 nm, −61.9 mJ/m^2, respectively). HDPE was cleaned more efficiently by Model cleaning solution B than Model cleaning solution A at all concentrations of peanut butter (0.001 % - 10 %). Recovery of the retained protein from the surfaces using Enzyme-Linked Immunosorbent Assay (ELISA) demonstrated that on the stainless steel, regardless of the cleaner or concentration used, no allergen was detected on the surface. The HDPE surfaces detected allergen from surfaces fouled with 10 % and 1 % peanut butter (5.12 ppm – 11.6 ppm and 0.01 ppm – 0.9 ppm, respectively). The recovery of allergens suggests an effect of the surface free energy and size of the surfactant molecules. Such findings are important when considering the selection of cleaners with respect to cleaning and allergen removal.

1. Introduction

Within any food processing industry, one of the major concerns is maintaining excellent hygiene. Good food hygiene is necessary for a variety of reasons, including maintenance of food quality and food safety, for example, removal of food fouling from surfaces to prevent contamination and removal of allergens (Johansson and Somasundaran, 2007). The food industry exposes its food products during their production and packaging to a variety of different surfaces. Most food soils are heterogeneous and complex, and they can be multicomponent and micro-structured, and oils have been found to be difficult to remove from surfaces due to their hydrophobicity (Cuckston et al., 2019). Food soils vary in composition, and no single wet-cleaning protocol is ideal for all situations (Jackson et al., 2008). The manner in which a soil is removed from the surface will be dependent on the internal cohesion of the food molecules present in the soil, and its adhesion to the surface. Hence, detergent design is important since it will affect the strength of binding that dictates soil adhesion and cohesion. The removal of oils from a surface can be achieved using surfactants which break oils into smaller droplets through the reduction of oil-water interfacial tension. Surfactants can be used to alter the adhesion and cohesion forces that bind the soil together and adhere a food soil to a surface by changing the surface tension so that the forces between the soil and substrate become more hydrophilic (Landel and Wilson, 2021). Removal of protein films requires alkali-based (i.e., sodium or potassium hydroxide) detergents (Schmidt, 1997), or a combination of alkalinity together with an oxidising agent such as sodium hypochlorite. Although sequential production planning is important, cleaning is considered the first line of defence against allergen cross-contact in shared processing lines (Jackson et al., 2008). However, research on the efficacy of cleaning of surfaces is heavily focused on the removal of microorganisms, rather than on the removal of allergenic material (Bedford et al., 2020).

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Consumers with food allergies rely on food labels to disclose the presence of allergenic ingredients; however, undeclared allergens can be inadvertently introduced into food via cross-contact during manufacturing, and this can occur at any stage during food production and storage (Jackson et al., 2007). From a practical economic perspective, in some instances, the food industry must manufacture many different food products within the same manufacturing facility (Taylor et al., 2002). Cross contamination of nut traces can occur, and it has been shown using real-time PCR from the analysis of 229 commercial food products that 29 did not declare pistachio or traces on the label, but samples were found to contain pistachio (López-Calleja et al., 2014). The presence of cleaning products can add a further level of complexity to understanding interactions at the protein:surface interface. Inadequate cleaning of processing equipment has been suggested to be responsible for the presence of undeclared peanut residues in ice cream and bakery products (Jackson et al., 2007). Another study has shown that 25 % of sampled ice cream, bakery, and candy food products were positive (>10 ppm) for undeclared peanut protein (Jackson et al., 2008). Hence, it is important to understand how allergenic material can be removed from different types of surfaces that might be used in the food industry. The removal of allergens is important, particularly from food contact surfaces, since the levels of allergenic protein required to trigger a reaction can be low. Enzyme-Linked Immunosorbent Assay (ELISA) can be used to quantify the residual allergenic protein that could be recovered from the surfaces, and it is the most frequently used analytical method to detect nut allergens (Akkerdas et al., 2004; Kiening et al., 2005; Ben Rejeb et al., 2005). One way to consider the levels of allergenic protein required to trigger a reaction in an allergenic person is via the VITAL Scientific Expert Panel recommendations, which summarise different individual challenge studies to obtain a recommended dose where less than 95 % and 99 % of allergenic people will not have a response (Allergen Bureau, 2019). The prevalence of clinical allergy to peanuts and nuts is estimated at about 0.4 % - 1.1 % in the adult population (EFSA, 2014). It has been demonstrated in 1306 individual peanut challenge studies that thresholds of 2.1 mg were needed to trigger less than 5 % of the allergenic population and 0.2 mg to trigger less than 1 % of the population (Allergy Bureau, 2019). Undeclared nut products may be present in food due to cross-contamination. This issue arises from their potential to cause allergic reactions and the legal requirement to label food products for allergenic components, including nuts. (López-Calleja et al., 2014; European Commission, 2011).

Peanuts are a widely consumed food that are rich in components. One of the most commonly consumed forms of processed peanuts is peanut butter, a food spread made from ground, dry-roasted peanuts. Peanut butter is composed of approximately 50 % fat, ~20–25 % protein and ~20–25 % carbohydrates along with dietary fibre, antioxidants and other compounds (Arya et al., 2016; U.S. Department of Agriculture, 2020). Peanut butter contains a significant number of vitamins and minerals, and it is known that calcium and magnesium, of which peanut butter tends to contain around 49 mg/100 g calcium and 169 mg/100 g magnesium (U.S. Department of Agriculture, 2020), are particularly difficult to remove from surfaces because they are prone to nucleation and form numerous small calcium phosphate aggregates in the initial stage of fouling (Detry et al., 2010). This occurs more on polar surfaces, resulting in more compact deposit structures that are harder to remove from the substrate (Detry et al., 2010). It is also known that fouling deposits often include mineral salts, and that calcium ions play an important role in the interactions between proteins and their denaturation and aggregation (Belmar-Beiny & Fryer, 1993; Saget et al., 2021). Peanut butter contains water, but compared with the three main components, it is minimal and is typically only around 1 % of the total makeup of the nutritional peanut butter composition (Arya et al., 2016). Peanut butter was selected as a model soil in this work since it is chemically complex with a high oil and protein content, which makes it potentially difficult to remove from the surface. In addition, it contains a major food allergen (Arya et al., 2016).

The aim of this fundamental work was to understand how two detergents with chemically different surfactants affected the removal of peanut butter from two chemically different surfaces, stainless steel and HDPE, and how these factors affected the recovery of allergenic protein from the surfaces following cleaning.

2. Methods

2.1. Coupon Preparation

304 Grade 2B stainless steel (Aalco, Bolton, UK) or High-Density Polyethylene (HDPE) (Plastic Sheets, Leicester, UK) coupons were cut into 20 mm x 20 mm square coupons using a guillotine (Cidan Rapido 13, Götene, Sweden) by placing 1 m x 1 m sized, 1.0 mm thick sheets of stainless steel into the machine, cutting strips length ways, and then cutting the lengths into individual coupons. The cut coupons were cleaned by submersion into acetone (BDH, Leicestershire, UK) for 10 min, methanol (BDH, Leicestershire, UK) for 10 min, and ethanol (BDH, Leicestershire, UK) for 10 min, with coupons being rinsed by submersion into sterile distilled water between each step and a final rinse after the ethanol wash before being air dried. The coupons were stored in clear containers at room temperature and were used within 7 days of storage.

2.2. Cleaning Solutions

The cleaning solutions chosen were selected to compare a cleaner that is commonly used in industrial premises with two basic formulations to demonstrate the effect that different commercially available surfactants can have on the efficacy of cleaning products. The surfactant used in Product A was a more commonly used and cheaper surfactant, whereas the surfactant used in Product B was a more expensive and chemically different surfactant. The cleaning solutions used in this work included a commercially available low-caustic foam detergent for open plant cleaning, which contained a mix of surfactants, emulsifiers, ethylenediaminetetraacetic acid (EDTA), and foaming agents, and had an in-use pH of around 12.5. In addition, two formulations were made, both of which contained the same solubiliser, an ethoxylated iso-tridecanol alcohol non-ionic surfactant with 6 moles of ethoxylation (BASF, UK). Both cleaners were made up to a pH 13 in distilled water and buffered using NaOH (INEOS, UK) or HNO_3 (Airdale, UK). The cleaner termed Model cleaning solution A contained an anionic surfactant (sodium salt of dodecyl benzene sulphonic acid (Surfachem, Bradford)) and EDTA (BASF, UK). Model cleaning solution B, which was anionic at pH 13, contained a short-chain alkyl ether carboxylate with 4 moles of ethoxylation (Kao Chemicals, UK) and EDTA (Table 1).

Table 1
Composition of cleaning agents used in this study.

Product	Description	Surfactants	Other components	pH
Commercial cleaner	Low-caustic foam detergent	Mix of surfactants	Emulsifiers, EDTA, foaming agents	12.5
Product A	Anionic surfactant	Sodium salt of dodecyl benzene sulphonic acid which had a medium (*circa* C12) hydrophobic and a large hydrophilic chemical moiety.	EDTA	13
Product B	Anionic surfactant	Short chain alkyl ether carboxylate with 4 moles of ethoxylation with a small hydrophobic moiety.	EDTA	13

2.3. Preparation of Coupons with Detergent for Physicochemical Analysis

Thirty millilitres of commercial cleaner, Model cleaning solution A or Model cleaning solution B was poured into clean Petri dishes containing stainless steel or HDPE coupons that had been secured to the bottom of the Petri dish using double-sided tape. After 30 min, the coupons were removed from the solutions and dipped into clean water to remove excess detergent. The coupons were air-dried for 1 h ($n = 3$).

2.4. Physicochemical Analysis of Surfaces

The left and right side contact angles (θ) were measured using HPLC grade water (BDH, Leicestershire, UK), ethylene glycol (Thermo Fisher, Loughborough, UK) or dioodomethane (Thermo Fisher, Loughborough, UK) using a goniometer (MobileDrop, Krüss GMBH, Hamburg, Germany) ($n = 10$). Before the use of each solvent, fresh coupons were used. The surface energy (γ_s^{SE}) was calculated according to van Oss et al. (1988):

$$(1 + \quad \gamma_l)\cos\theta = 2 \quad \left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \quad \sqrt{\gamma_s^{A}\gamma_l^{B}} + \quad \sqrt{\gamma_s^{B}\gamma_l^{A}}\right) \tag{1}$$

where s denotes the surface energy of the solid and l the surface energy of the liquid. LW is the Lifshitz-van der Waals component of the surface energy, A is the Lewis acid and B the Lewis base parameters. The acid and base components can be used to determine the polar component of the surface energy (2):

$$\gamma_i^{AB} = \quad 2\sqrt{\gamma_i^{A}\gamma_i^{B}} \tag{2}$$

The sum of the Lifshitz-van der Waals and Lewis acid base properties were used to determine the surface energy (3):

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \tag{3}$$

The hydrophobicity was calculated using the surface free energy components (van Oss and Giese, 1995):

$$\Delta G_{sw} = -2 \quad \left(\left(\sqrt{\gamma_s^{LW}} - \sqrt{\gamma_w^{LW}}\right)^2 + 2 \quad \left(\sqrt{\gamma_s^{a}\gamma_s^{b}} + \sqrt{\gamma_w^{a}\gamma_w^{b}} - \sqrt{\gamma_s^{a}\gamma_w^{b}} - \sqrt{\gamma_w^{a}\gamma_s^{b}}\right)\right) \tag{4}$$

2.5. Surface Roughness

Surface roughness profiles and the average of the mean centre points (S_a and S_{pv}) values were calculated from surface profiles measured using a ZeGage 3D Optical Surface Profiler (Zygo, Middlefield, CT, USA) for the stainless steel and HDPE coupons. S_a is an extension of R_a (arithmetical mean height of a line) to a surface; however, measurement points are taken across the entire surface rather than just a mean centre line. S_{pv} measures the distance between the highest and lowest points within a sampled three-dimensional (3D) area. Measurements were taken at 50 x magnification, with a scanning distance of 50 μm from the centre position ($n = 3$). The scan area was 160 μm x 160 μm and the effective resolution was 886 px/mm.

2.6. Peanut Butter Suspension Preparation

A 10 % (w/v) suspension of peanut butter (Sunpat Peanut Butter Smooth, Hain Celestial Group, London, UK), which was stored at room temperature in the dark, was prepared by mixing 5 g of peanut butter with 45 mL of distilled water, and mixed on a plate stirrer at 50 °C until the peanut butter was fully suspended in the water. The suspension was diluted to concentrations of 1 %, 0.1 %, 0.01 % and 0.001 % (w/v) peanut butter.

2.7. Soak Clean of the Fouled Surfaces

The surfaces were fouled with the appropriate concentration of peanut butter, dried at room temperature for 1 h, and then submerged into 30 mL of either the commercial cleaner, Model A cleaning solution, or Model cleaning solution B. The fouled surfaces were left to soak for 30 min without agitation at room temperature. Removal of the coupons from the solution was carried out using clean forceps. The unfouled surfaces were rinsed in clean distilled water and air-dried for 1 h.

2.8. Epifluorescence Staining and Microscopy of the Surfaces

Following fouling and cleaning of the surfaces, the surfaces were flooded with 500 μL of 0.03 % acridine orange (Sigma-Aldrich, Dorset, UK) and left to stain for 2 min. The surfaces were submerged into sterile distilled water and immediately rinsed. The coupons were dried for 1 h in the dark in a class 2 flow hood. The stained samples were imaged using an epifluorescence microscope (Nikon Eclipse E600, London, UK). The percent coverage of fouling was determined using intensity profiling. The image thresholding was carried out by taking the gray-scale image that was captured by the camera. This was converted into a binary image by determining the pixel value as either black or white based on its intensity level compared to the threshold value set on the microscope. For each cleaning variable tested, three individual surfaces were used. For each of the three replicate surfaces, ten images were taken to determine the percentage coverage of fouling across the surfaces.

2.9. Enzyme-Linked Immunosorbent Assay (ELISA)

The surfaces were fouled and cleaned as previously described. The allergen was removed from each surface by swabbing using swabs provided in a Protein Surface-Check Swabbing Kit (Bio-Check, Denbighshire, UK), which has a limit of quantitation of 1 mg – 30 mg allergen/kg (ppm) and a limit of detection of < 0.5 mg allergen/kg (ppm). The surfaces were rotated whilst swabbing in 3 directions. The swabs were stored in tubes containing storage media as part of the Surface-Check Swabbing Kit (Bio-Check, Denbighshire, UK) and vortexed for 10 s. Recovered allergen was determined using the Peanut Check Kit (Bio-Check, Denbighshire, UK) according to the manufacturer procedures.

2.10. Statistical Analysis

Statistical analysis was performed using the IBM SPSS Statistics version 28 for Windows (IBM SPSS, Inc., Chicago, IL, USA). Data was quantified using the mean values and the standard error of the mean was displayed to demonstrate the deviation from the sample mean. For each concentration of peanut butter (10 %, 1 %, 0.1 %, 0.01 %, or 0.001 % (w/v)), significant differences across the cleaning treatment types (PB Control, Water, Commercial, Model A, and Model B) were determined using a one-way analysis of variance (ANOVA) and were considered significant at the 95 % confidence level whereby $p < 0.05$. A Post Hoc Tukey's HSD (Honestly Significant Difference) test was performed to define differences between means (Table 1S-8S of Supplementary Material). When necessary, the same type of test was applied to compare the means between stainless steel and HDPE.

3. Results

3.1. Physicochemistry of the Surfaces

The physicochemical data (Table 2) demonstrated distinct differences between the stainless steel and HDPE surfaces. The stainless steel demonstrated a Gibbs Free energy result of −4.5 mJ/m^2, indicating that the surface was less hydrophobic than the HDPE surface (-61.9 mJ/m^2).

Table 2 -
Physicochemistry of stainless steel and HDPE surfaces demonstrating Gibbs Free energy, Total Free energy, Lifshitz van der Waals, Lewis Acid-Base, Lewis Acid and Lewis Base values, and following immersion in commercial detergent, Model cleaning solution A or Model cleaning solution B. Values are in mJ/m^2.

	Gibbs Free energy (ΔG_{iwi})	Total Free energy (γ_s)	Lifshitz van der Waals (γ_{LW})	Lewis Acid-Base (γ_{AB})	Lewis Acid (γ^+)	Lewis Base (γ^-)
Stainless steel	−4.5	42.6	38.7	3.9	0.3	27.4
HDPE	−61.9	38.3	35.6	2.7	0.9	3.6
					Gibbs Free energy (ΔG_{iwi})	Lewis Base (γ^-)
Stainless steel with commercial cleaner					27.5	44.7
Stainless steel with Model cleaning solution A					31.9	52.4
Stainless steel with Model cleaning solution B					44.7	59.6
HDPE with commercial cleaner					9.6	40.2
HDPE with Model cleaning solution A					−41.3	10.9
HDPE with Model cleaning solution B					−35.2	11.5

The stainless steel surfaces and HDPE surfaces demonstrated similar total energy (42.6 mJ/m^2 and 38.3 mJ/m^2), which was made up of the dispersive van der Waals component (38.7 mJ/m^2 and 35.6 mJ/m^2) and the polar Lewis acid-base component (3.9 mJ/m^2 and 2.7 mJ/m^2).

The polar component for the two surfaces were different, being 0.3 mJ/m^2 and 0.9 mJ/m^2 for the acid or positive component, and 27.4 mJ/m^2 and 3.6 mJ/m^2 for the basic or negative component of the stainless steel and HDPE surfaces, respectively. This demonstrated that the stainless steel surfaces had a strong negative polar charge and the HDPE surfaces had acid and less basic surface components. Following soaking of the coupons in the cleaning solutions, it was demonstrated that for the Gibbs Free energy, all the stainless steel surfaces became more hydrophilic and had greater Lewis base component values when compared to the untreated surfaces.

3.2. Topography of the Surfaces

The two surfaces demonstrated significant differences in their surface roughness (Fig. 1), with the stainless steel surfaces demonstrating an average roughness (S_a) of 162.4 nm, which was significantly less than the average roughness of the HDPE surfaces (3261.4 nm). For the S_{pv} data, the same trend was demonstrated (S_{pv} of stainless steel = 2409.6 nm and S_{pv} of HDPE = 59980.0 nm).

3.3. Visualisation of the Retained Fouling on the Surfaces Following Cleaning

The epifluorescence images of the stainless steel surfaces (Fig. 2) fouled with 10 % peanut butter suspension demonstrated a significant amount of fouling covering the surface (Fig. 2 A-E), with the least fouled being those cleaned with the commercial cleaner (Fig. 2K-O). As the concentration was reduced, the amount of fouling covering each surface also decreased. Following fouling with all the concentrations of peanut butter, the commercial cleaner washed surfaces appeared all to have significantly less fouling coverage. Visually, the fouling left retained on the surfaces following cleaning at concentrations ≤ 1 % with Model cleaning solution A (Fig. 2P-T) or Model cleaning solution B (Fig. 2U-Y) looked to be similar.

When the surfaces were imaged to measure the retained fouling on the HDPE surfaces (Fig. 2AA-YY), the HDPE surface fouled with 10 % peanut butter demonstrated a significant amount of fouling (Fig. 2AA). The surfaces cleaned with commercial cleaner had the least amount of fouling present (Fig. 2KK - OO). As expected for all surfaces, as the concentration of peanut butter reduced, the amount of foulant covering each surface was also reduced. When the HDPE surface was fouled with a 0.001 % concentration of peanut butter, the surfaces cleaned by any of the three detergents (commercial cleaner, Fig. 2OO; Model cleaning solution A, Fig. 2TT; and Model cleaning solution B, Fig. 2YY) looked to be almost nothing present on the surface when compared to the peanut butter control.

3.4. Percent Coverage

The use of peanut butter at different concentrations demonstrated differences in the amount of fouling coverage on the stainless steel (Fig. 3 A) and HDPE surfaces (Fig. 3B). A trend of reduced foulant coverage of the stainless steel surfaces was quantified as the concentration reduced for all the samples.

When fouled stainless steel surfaces were cleaned using just water, there was a significant reduction in the amount of surface covered at 1 % or 0.001 % concentrations compared to control ($p < 0.001$). Contrary, there were no significant differences in peanut butter concentrations remaining when peanut butter concentrations of 10 %, 0.1 %, or 0.01 % had been applied and removed from the surfaces compared to the control surfaces ($p > 0.05$). The greatest reductions in surface coverage were obtained with the commercial cleaner, which demonstrated significant reductions at all peanut butter concentrations ($p < 0.001$).

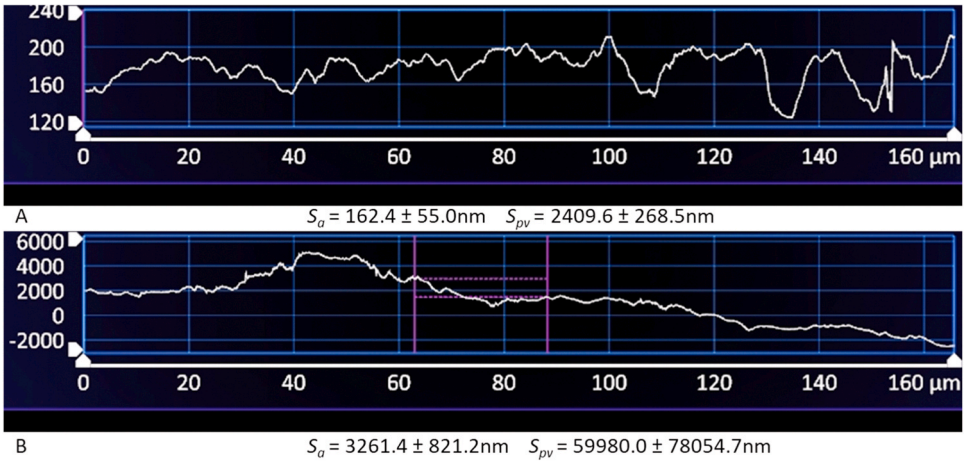

Fig. 1. – Line profiles to demonstrate the surface features and surface roughness values (S_a and S_{pv}) for A) stainless steel and B) HDPE surfaces. Note the difference in the height of the y axis.

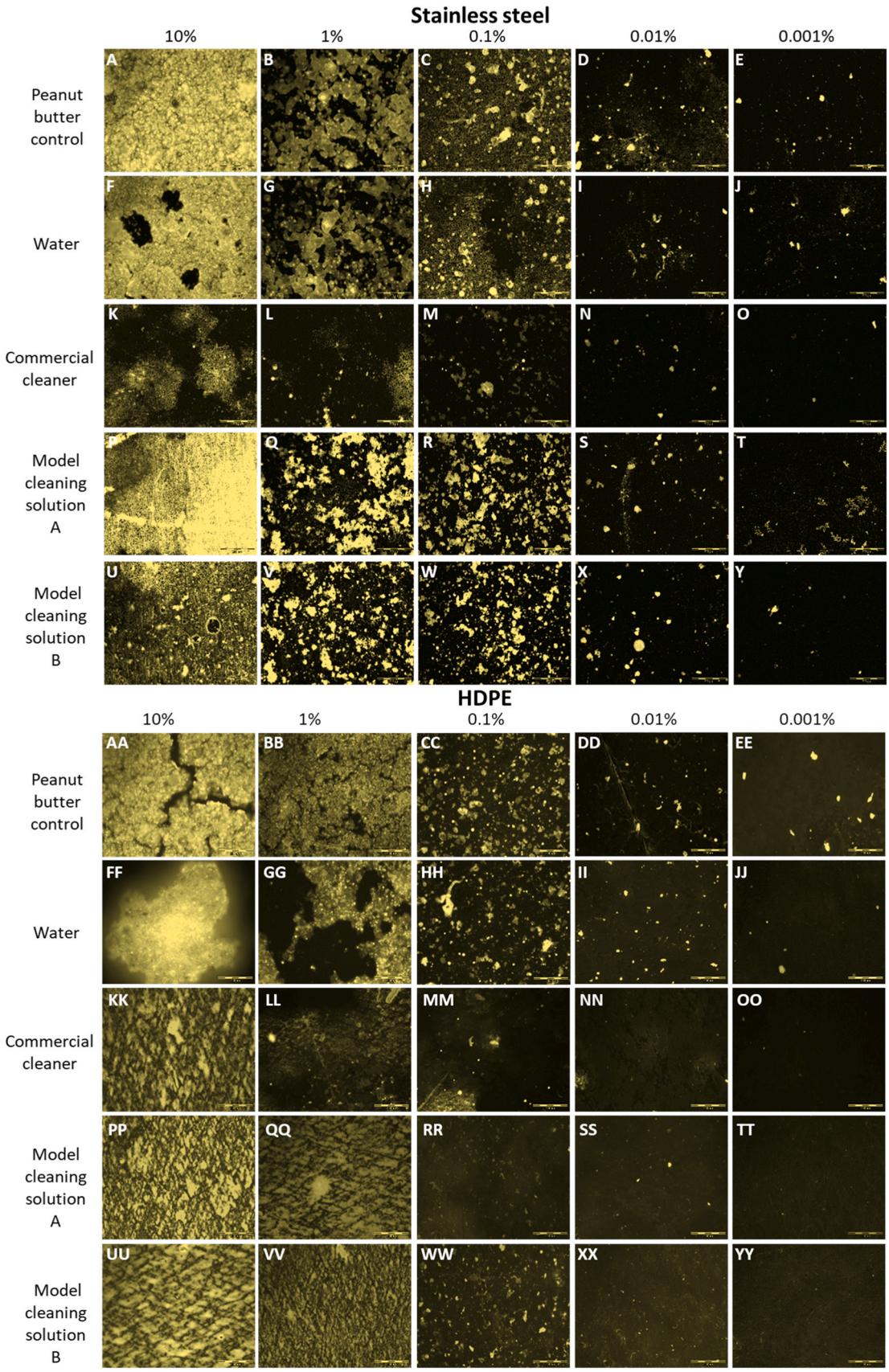

Fig. 2. - Coverage of retained foulant on A-Y) stainless steel and AA-YY) HDPE surfaces following application of peanut butter at concentrations of 10 %, 1 %, 0.1 %, 0.01 % and 0.001 % (w/v) demonstrating either no cleaning (Peanut butter control) or cleaning using water, 4 % commercial cleaner, Model cleaning solution A or Model cleaning solution B.

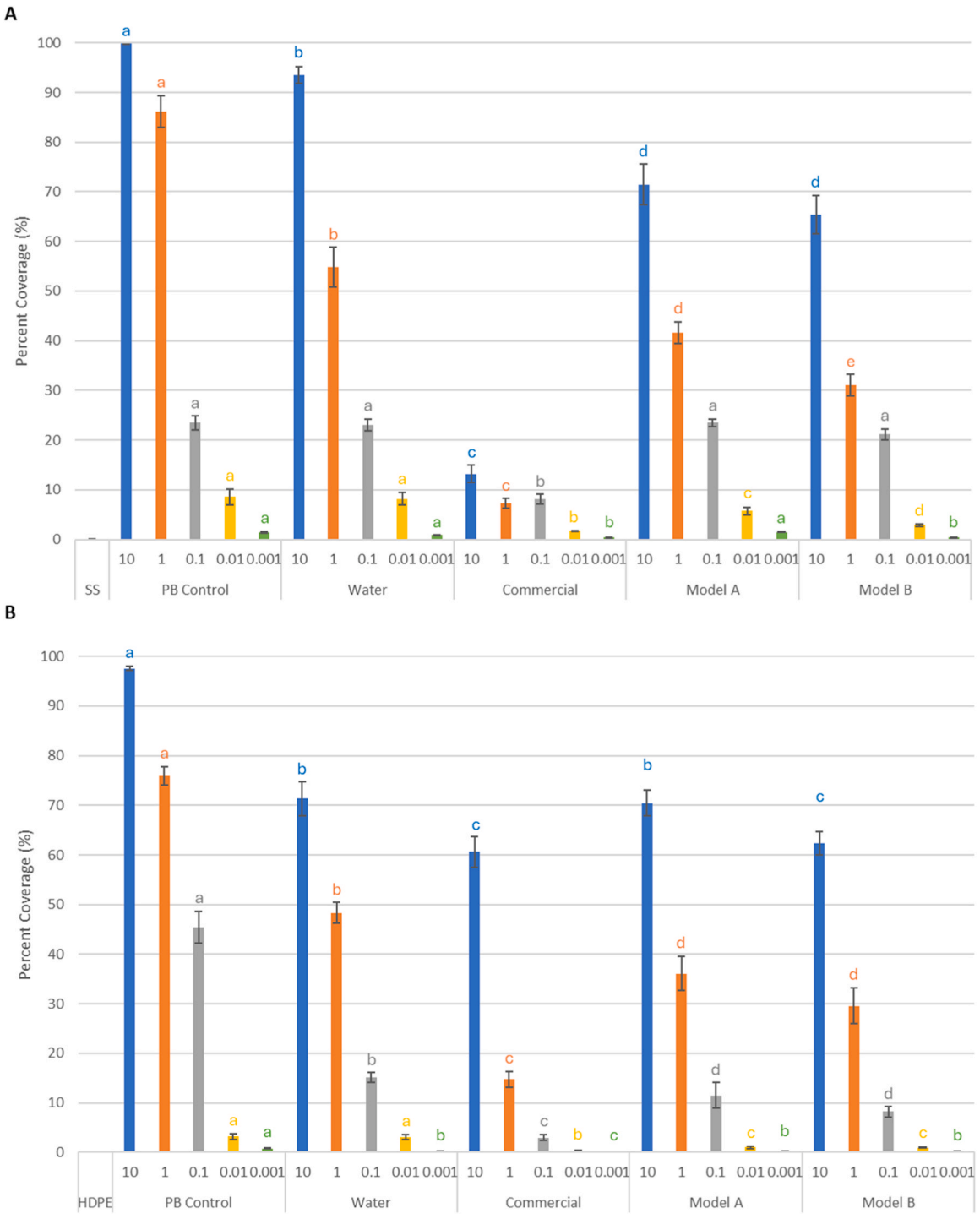

Fig. 3. - Percent coverage of A) stainless steel and B) HDPE surfaces after fouling with peanut butter diluted to 10 % (blue bars), 1 % (orange bars), 0.1 % (grey bars), 0.01 % (yellow bars) and 0.001 % (w/v) (green bars) and cleaned using either water, 4 % commercial cleaner, the Model detergent A or the Model detergent B plus unfouled and fouled controls, as determined via epifluorescence imaging. For each fouling concentration (10 %, 1 %, 0.1 %, 0.01 % or 0.001 % (w/v)), different lowercase letters indicate statistically significant differences between treatments ($p < 0.05$).

When cleaned with either of the model detergents, the amount of peanut butter covering the surfaces was reduced at higher concentrations of 10 % and 1 %. When a suspension of 0.1 % peanut butter was applied to the surfaces, neither of the solutions demonstrated any significant difference to the control ($p > 0.05$), and at 0.001 %, only the Model B detergent demonstrated a reduction in coverage ($p < 0.001$).

When the percent coverage of retained fouling was determined on HDPE (Fig. 3B), the results demonstrated that there was significant difference compared to the control for all the cleaners. Following cleaning of the surface which had 0.01 % peanut butter fouling, there was a significant difference in the amount of peanut butter removed from the surfaces using the commercial cleaner, Model cleaning solution A and Model cleaning solution B compared to the control surface.

When the results for the equivalent concentrations of fouling and cleaning were compared between the stainless steel and HDPE surfaces, it was demonstrated that there were significant differences in the results

between the two surfaces with all cleaners at all concentrations ($p < 0.001$). However, following the use of the commercial cleaner, at 10 % and 1 % concentrations, fouling was significantly less on the stainless steel surfaces. At concentrations of 0.1 %, 0.01 % and 0.001 %, fouling was significantly less on the HDPE surfaces cleaned with the commercial cleaner. After use of Model cleaning solution A or Model cleaning solution B, regardless of the fouling concentration, there was less fouling on the HDPE surfaces.

3.5. ELISA Analysis of the Surfaces to Recover Allergenic Protein

The ELISA results for the stainless steel surfaces fouled with peanut butter (Fig. 4 A) demonstrated that, for the control surfaces, when concentrations of 10 %, 1 % or 0.1 % (w/v) were used, the amount of peanut protein recovered reached the upper limit of the instrument detection threshold. When rinsed using water, only the 10 % and 1 % suspensions had recovered protein at the edge of the detection capabilities of the spectrophotometer, whilst the 0.1 %, 0.01 %, and 0.001 % suspensions demonstrated a recovery of 54 ppm, 12 ppm and 9.6 ppm allergen, respectively. However, when concentrations of 10 %, 1 %, 0.1 %, 0.01 % and 0.001 % were cleaned with any of the detergent, no allergen was recovered from the surfaces.

The ELISA results for HDPE surfaces fouled with peanut butter (Fig. 4B) demonstrated that the control fouled surfaces and surfaces cleaned with water from the surfaces fouled with 10 %, 1 % and 0.1 % peanut butter had significantly lower allergen recovery than was obtained from the stainless steel surfaces ($p < 0.001$). When detergents were used to clean the fouled surfaces, none of the detergents resulted in recoverable allergens when used on peanut butter concentrations of 0.1 %, 0.01 % and 0.001 %. However, when the peanut butter concentration was at 10 %, all the detergents demonstrated recoverable allergenic protein on HDPE with the commercial cleaner having the least recovered (5.1 ppm) followed by the Model cleaning solution B (6.4 ppm) with the Model cleaning solution A having the greatest amount of peanut allergen recovered (11.6 ppm $p < 0.02$). When the peanut butter suspension was used to foul the surfaces at 1 %, the same

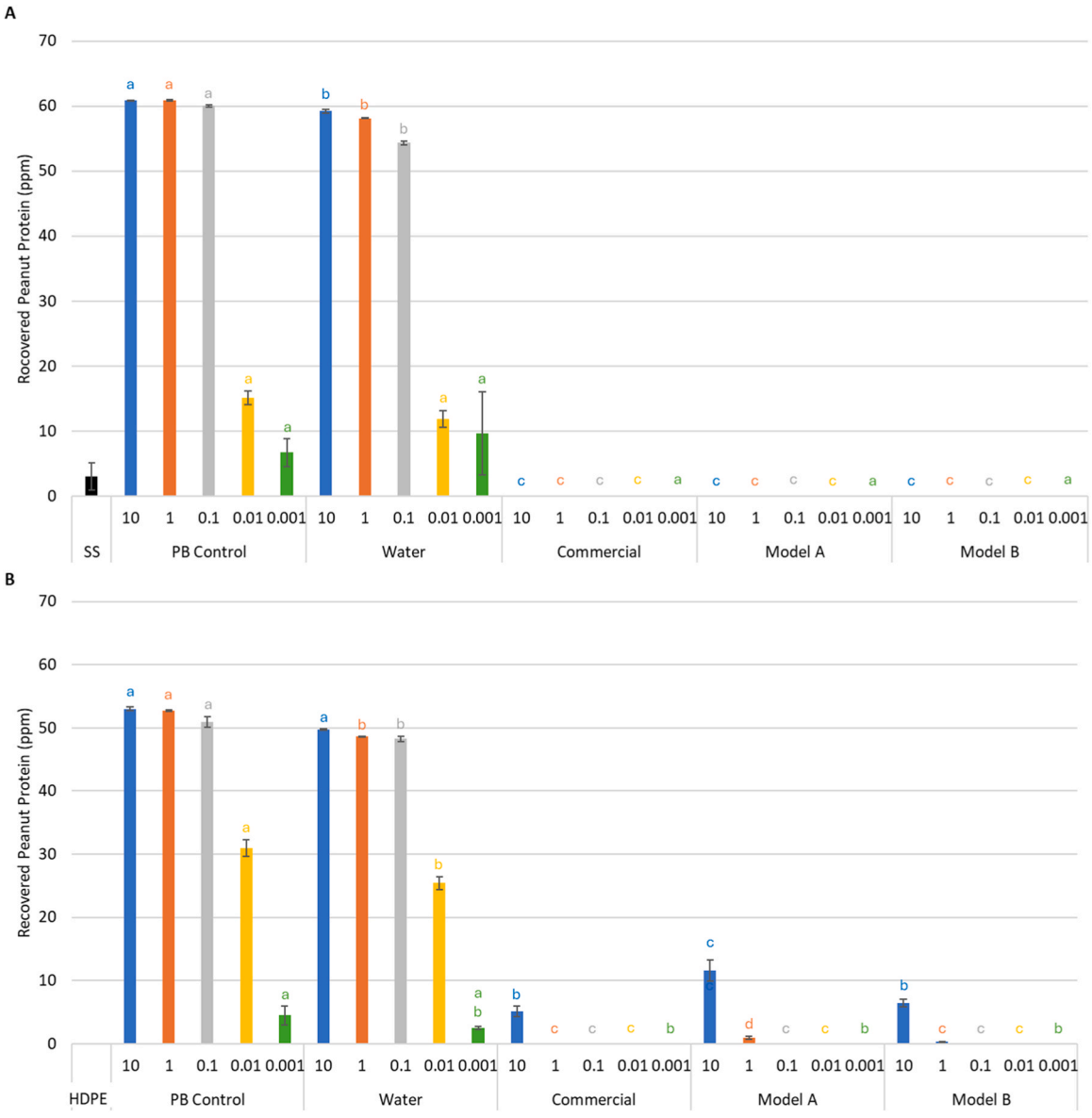

Fig. 4. - Amount of peanut recovered from A) stainless steel and B) HDPE surfaces fouled with peanut butter diluted to 10 % (blue bars), 1 % (orange bars), 0.1 % (grey bars), 0.01 % (yellow bars) and 0.001 % (w/v) (green bars) and cleaned either water, 4 % commercial cleaner, the Model detergent A or the Model detergent B. For each fouling concentration (10 %, 1 %, 0.1 %, 0.01 % or 0.001 % (w/v)), different lowercase letters indicate statistically significant differences between treatments ($p < 0.05$).

trend was observed with the least protein recovered using the commercial cleaner (0.01 ppm), followed by Model cleaning solution B (0.3 ppm), and then the Model cleaning solution A (0.9 ppm).

4. Discussion

Cleaning is used to maintain the hygienic conditions in food preparation industries. However, the complex interactions between the cleaner components, the food soil and the surfaces are not well understood. Most food soils are heterogeneous and complex, and they can be multicomponent and micro-structured, and oils have been found to be difficult to remove from surfaces due to their hydrophobicity (Cuckston et al., 2019). The manner in which a soil is removed from the surface will be dependent on the internal cohesion of the food molecules present in the soil, and its adhesion to the surface. Hence, detergent design is important since this will affect the strength of binding that dictates soil adhesion and cohesion (Cuckston et al., 2019). Surfactants can be used to alter the adhesion and cohesion forces that bind the soil together and adhere a food soil to a surface by changing the surface tension so that the forces between the soil and substrate become more hydrophilic (Landel and Wilson, 2021). Although food soils adhere to a surface through a combination of physicochemical forces, e.g., Lifshitz-van der Waals, ionic and electrostatic forces (Moeller and Nirschl, 2017), the changes in wetting behaviour due to addition of surfactants to a detergent solution can lead to food soil removal. Model cleaning solution A contained an anionic surfactant which had a medium (*circa* C12) hydrophobic and a large hydrophilic chemical moiety. Model cleaning solution B contained a short chain alkyl ether carboxylate with 4 moles of ethoxylation with a small hydrophobic moiety. The results demonstrated a non-linear trend of increased efficacy of the detergents as the concentration of the peanut butter foulant was reduced. In addition to a mix of non-ionic, anionic and amphoteric surfactants, the commercial agent also contained foaming and anti-scale deposition agents.

Following cleaning of the stainless steel, residual food soil on the surfaces was left behind. This may have occurred if the interfacial tension of the oil:water interface decreased, but at the solid:water interface, it was not substantially affected. This could have resulted in bulk cohesive failure whereby the removal of the food soil was due to the cohesive forces inside the food soil breaking down, leaving some soil deposit on the surface (Fryer and Asteriadou, 2009).

Surfactants work by decreasing the surface tension at the surface:soil interface. Once a detergent becomes adsorbed to a surface, to regain equilibrium, the contact angle decreases and as the hydrophilicity of the surface continues to decrease, then the surfactant becomes energetically preferable to adsorb to the surface. If these energies become sufficiently reduced, then the surface tension cannot increase enough to reach the energetic equilibrium required by the soil at the soil:interface to become re-adsorbed, and so the soil becomes displaced (Davies and Rideal, 1961). Although this phenomenon was observed on the HDPE surface, it was not observed on the stainless steel surface. An alternative explanation could be in part due to the physicochemical nature of the surfaces. It has been demonstrated that surfaces with different surface energies result in deposits with different structures and resistance to removal (Rosmaninho and Melo, 2006; Detry et al., 2010). The stainless steel surface was more hydrophilic than the HDPE surface, with a greater surface free energy, Lifshitz van der Walls, acid base and electron donor properties. The surface free energy for HDPE can range between 28 and 36 mN/m (Globalspec, 2024; Reylon, 2024) whereas for stainless steel, there have been values reported as varied as between 39 and 45 mN/m Williams et al., 2017; Avila-Sierra et al., 2019). Therefore, our results are within the reported ranges for stainless steel and marginally higher for HDPE. In agreement with these results, it has been shown that the amount of soil adhering to a substrate was increased with its polarity (Michalski et al., 1999). Rosmaninho and Melo (2006) demonstrated that using a simulated milk ultrafiltrate, there was a positive correlation between the amount of deposit and surfaces with a higher γ^- component, which is in agreement with the results demonstrated in this study.

The two surfaces used in this study varied greatly in terms of their roughness, chemistry and physicochemistry. There has been much debate regarding how to accurately determine the physicochemistry of a rough surface. Although there has been much discussion regarding whether the Wenzel or Cassie Baxter equations are best to use with a roughened surface, there is a lack of clarity regarding at which point the transition between the Wenzel and Cassie Baxter equations occurs, and thus, it is not clear under what circumstances these equations are valid. The problems in part are related to the discussion of whether the wetting of surfaces is a 1D process, which is determined by thermodynamic equations for the free surface energies, or a 2D process, which is described by the kinetics of the solid-liquid-vapor contact line (triple line) and surface tension (Nosonovsky and Bhushan, 2008). Gao and McCarthy (2007) have showed experimentally that the contact angle of a droplet is defined by the triple line and does not depend upon the roughness under the bulk of the droplet; thus, they concluded that the Wenzel and Cassie equations "should be used with the knowledge of their fault". Hence, the results given within this study are of value within the tested parameters.

When surfaces cleaned using detergents were swabbed for recoverable allergenic protein, the stainless steel surface demonstrated no allergenic protein recovery for any detergent. However, from the epifluorescence images, it was clear that the peanut butter fouling was still present on the surfaces. This suggested that either the fouling visible in the epifluorescence images was not protein, or that the allergenic peanut protein present was so strongly bound to the stainless steel surfaces that it could not be removed. In contrast, HDPE surfaces demonstrated recoverable allergenic protein on surfaces fouled with higher concentrations of peanut butter. One explanation might be that the protein was removed from the HDPE more easily than the stainless steel since on surfaces with higher surface energy, proteins are more likely to become denatured, hence promoting changes in their conformational states (Rosmaninho and Melo, 2006) and therefore less easy to remove. Another factor may be that the chemistry of the underlying surface affected the strength of the binding of the peanut butter at higher concentrations. HDPE is composed of saturated nonpolar alkane chains, thus lacking the ability to interact with a protein via either hydrogen bonding or electrostatic effects, while having the potential to exhibit strong hydrophobic interactions with the hydrophobic amino acid residues of a protein (Thyparambil, 2015). The HDPE was much more hydrophobic with significantly lower Lewis base and electron donor components than the stainless steel, so maybe the proteins may have been more easily removed.

There may also be a chemical effect that affected allergen removal due to the surface properties of the stainless steel. Once applied, the protein will interact with the surface via electrostatic, van der Waals and hydrophobic interactions, which will influence its adsorption onto the surface (Chandrasekaran and Ramachandran, 1970). As the protein is adsorbed, if fully reversible, desorption can occur, the proximity of the protein backbone to the substrate can create a stronger interaction with the surface (Roach et al., 2005; Yang and Etzel,2003). This can lead to protein denaturation and loss of biological function (Chandrasekaran and Ramachandran, 1970), and may also lead to an increased number of bonds available and greater adsorption to the underlying surface.

The roughness of the surfaces may also have affected the removal of the peanut butter from the surfaces. The topography of the stainless steel demonstrated smaller differences in the S_a and peak-to-valley heights (S_{pv}) when compared to HDPE. Work by others has demonstrated that with increasing roughness, there is a decrease in cleaning efficiency in immersed systems (Hauser, 2008). It has been suggested that fouling on rougher surfaces will be more protected from the mechanical and chemical actions of the cleaning fluid, and may escape cleaning and disinfection procedures (Detry et al., 2010; Hofmann and Sommer, 2006). Although the S_a and S_{pv} values provide information on the vertical distribution of surface roughness (z-axis), this does not provide

information to describe the spatial distribution or the spatial length scale of the roughness values (Gong et al., 2016). In such cases whereby the surface topography was greater on the HDPE, it is difficult to access the size of the surface microfeatures and if they are of similar sizes to those found on the stainless steel surfaces. Power spectral density (PSD) analysis, which are often used in the characterization of optical surfaces, provide both lateral and vertical signals (Gong et al., 2016), and in its two-dimensional form, it has been suggested that this is a parameter that should be included for specifying surface roughness (Elson and Bennett, 1995; ISO 10110, 1996). Such analysis would enable a comparison of the prominent topographies within the lateral scale, which would enable a better comparison of how the size of the surface features affected biofouling. However, such analysis still does not describe the shape of the surface features, which has also been shown to affect the extent of biological (microbial) binding (Whitehead et al., 2006; Verran et al., 2010).

5. Conclusion

The work used a complex soil which contained high levels of fats and proteins to determine how chemically different surfactants removed peanut butter from two different surfaces. The results demonstrated the importance of understanding the interaction of the chemistry of a detergent on the strength of soil and allergen removal for the development of cleaning solutions used in food processing industries. The originality and knowledge that was gained from this work was that surface properties and detergent composition influenced both the efficacy of cleaning and allergen removal from the surfaces, suggesting that one detergent will not optimally clean all surfaces. Hence, much more in depth work on the optimisation of cleaning solutions in relation to surface properties is required. More work is needed to introduce the Model solution B surfactant into complex commercial formulations to see if additional scientific understanding and optimisation of the Model solution can be achieved.

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CRediT authorship contribution statement

David Whitehead: Writing – review & editing, Investigation, Formal analysis, Data curation. **Kathryn Whitehead:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Joels Wilson-Nieuwenhuis:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Jim Taylour:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization. **Luciana C Gomes:** Writing – review & editing, Data curation.

Declaration of Competing Interest

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fbp.2024.12.002.

Data availability

Data will be made available on request.

References

Akkerdas, J.H., Wensing, M., Knulst, A.C., Stephan, O., Hefle, S.L., Aalberse, R.C., van Ree, R., 2004. A novel approach for the detection of potentially hazardous pepsin stable hazelnut proteins as contaminants in chocolate-based food. J. Agric. Food Chem. 52 (25), 7726–7731. https://doi.org/10.1021/jf049278r.

Allergen Bureau (2019) VITAL Scientific Expert Panel 2019 Summary Recommendations – the new allergen Reference Doses for VITAL® Program Version 3.0.

Arya, S.S., Salve, A.R., Chauhan, S., 2016. Peanuts as functional food: a review. J. Food Sci. Technol. 53 (1), 31–41. https://doi.org/10.1007/s13197-015-2007-9.

Avila-Sierra, A., Zhang, Z.J., Fryer, P.J., 2019. Effect of surface characteristics on cleaning performance for CIP system in food processing. Energy Procedia 161, 115–122. https://doi.org/10.1016/j.egypro.2019.02.067.

Bedford, B., Liggans, G., Williams, L., Jackson, L., 2020. Allergen removal and transfer with wiping and cleaning methods used in retail and food service establishments. J. Food Prot. 83 (7), 1248–1260. https://doi.org/10.4315/JFP-20-025.

Belmar-Beiny, M.T., Fryer, P.J., 1993. Preliminary stages of fouling from whey protein solutions. J. Dairy Res. 60 (4), 467–483. https://doi.org/10.1017/S0022029900027837.

Ben Rejeb, S., Abbott, M., Davies, D., Cléroux, C., Delahaut, P., 2005. Multi-allergen screening immunoassay for the detection of protein markers of peanut and four tree nuts in chocolate. Food Addit. Contam. 22 (8), 709–715. https://doi.org/10.1080/02652030500158450.

Chandrasekaran, R., Ramachandran, G.N., 1970. Studies on the conformation of amino acids. XI. Analysis of the observed side group conformation in proteins (doi/pdf/). Int. J. Protein Res. 2 (4), 223–233. https://doi.org/10.1111/j.1399-3011.1970.tb01679.x.

Cuckston, G.L., Alam, Z., Goodwin, J., Ward, G., Wilson, D.I., 2019. Quantifying the effect of solution formulation on the removal of soft solid food deposits from stainless steel substrates. J. Food Eng. 243, 22–32. https://doi.org/10.1016/j.jfoodeng.2018.08.018.

Davies, J.T., Rideal, E.K., 1961. Interfacial Phenomena, Second Ed. Academic Press.

Detry, J.G., Sindic, M., Deroanne, C., 2010. Hygiene and cleanability: a focus on surfaces. Crit. Rev. Food Sci. Nutr. 50 (7), 583–604. https://doi.org/10.1080/10408390802565913.

EFSA (2014) European Food Safety Authority Allergens in food: scientific advice updated EFSA Science, safe food, sustainability (europa.eu).

Elson, J.M., Bennett, J.M., 1995. Calculation of the power spectral density from surface profile data. Appl. Opt. 34 (1), 201–208. https://doi.org/10.1364/AO.34.000201.

European Commission (2011) Legislation 1169/2011/EC OJEU. Regulation (EU) No 1169/2011 Of The European Parliament And Of The Council of 25 October 2011. Official Journal of the European Union.

Fryer, P.J., Asteriadou, K., 2009. A prototype cleaning map: a classification of industrial cleaning processes. Trends Food Sci. Technol. 20, 255–262. https://doi.org/10.1016/j.tifs.2009.03.005.

Gao, L., McCarthy, T.J., 2007. How Wenzel and Cassie were wrong. Langmuir 23 (7), 3762–3765. https://doi.org/10.1021/la062634a.

Globalspec (2024) ⟨https://www.globalspec.com/reference/50610/203279/3-8-surface-properties⟩ (accessed November 2024).

Gong, Y., Misture, S.T., Gao, P., Mellott, N.P., 2016. Power spectral density (PSD) analysis provides both lateral and vertical signals. J. Phys. Chem. C. 120 (39), 22358–22364. https://doi.org/10.1021/acs.jpcc.6b06635.

Hauser, G., 2008. Hygiene gerechte Apparate und Anlagen: für die Lebensmittel-. Pharma- und Kosmetikindustrie. Wiley-VCH, Weinheim. ISBN: **978-3-527-32291-6**.

Hofmann, J., Sommer, K., 2006. Hygienic design von anlagen und deren qualifizierungsmethoden. Chem. Ing. Tech. 78, 1605–1614. https://doi.org/10.1002/cite.200600089.

ISO 10110 (1996) Optics and optical instruments—indications in optical drawings, in Draft International Standard ISO 10110:11 Surface Texture 1 International Organization for Standardization, ISO@TC 172@SC 1@WG 2, Geneva, Switzerland.

Jackson, L.S., Al-Taher, F.M., Moorman, M., Devries, J.W., Tippett, R., Swanson, K.M.J., Fu, T.-F., Salter, R., Dunaif, G., Estes, S., Albillos, S., Gendel, S.M., 2008. Cleaning and Other Control and Validation Strategies To Prevent Allergen Cross-Contact in Food-Processing Operations. J. Food Prot. 71 (2), 445–458. https://doi.org/10.4315/0362-028x-71.2.445.

Jackson, V., Blair, I.S., McDowell, D.A., Kennedy, J., Bolton, D.J., 2007. The incidence of significant foodborne pathogens in domestic refrigerators. Food Control 18 (4), 346–351. https://doi.org/10.1016/j.foodcont.2005.10.018.

Johansson, I., Somasundaran, P. (2007) Handbook for cleaning/decontamination of surfaces. 1st Edition, Volume 1. ISBN: 9780444516657.

Kiening, M., Niessner, R., Drs, E., Baumgartner, S., Krska, R., Bremer, M., Tomkies, V., Reece, P., Danks, C., Immer, U., Weller, M.G., 2005. Sandwich Immunoassays for the Determination of Peanut and Hazelnut Traces in Foods. J. Agric. Food Chem. 53 (9), 3321–3327. https://doi.org/10.1021/jf048394r.

Landel, J.R., Wilson, D.I., 2021. The fluid mechanics of cleaning and decontamination of surfaces. Annu. Rev. Fluid Mech. 53, 147–171. https://doi.org/10.1146/annurev-fluid-022820-113739.

López-Calleja, I.M., de la Cruz, S., González, I., García, T., Martín, R., 2014. Survey of undeclared allergenic pistachio (Pistacia vera) in commercial foods by hydrolysis probe real-time PCR. Food Control 39, 49–55. https://doi.org/10.1016/j.foodcont.2013.10.034.

Michalski, M.C., Desobry, S., Babak, V., Hardy, J., 1999. Adhesion of food emulsions to packaging and equipment surfaces. Colloids Surf. A. Physicochem. Eng. Asp. 149, 107–121. https://doi.org/10.1016/S0927-7757(98)00299-4.

Moeller, R.S., Nirschl, H., 2017. Adhesion and cleanability of surfaces in the baker's trade. J. Food Eng. 194, 99–108. https://doi.org/10.1016/j.jfoodeng.2016.09.012.

Nosonovsky, M., Bhushan, B., 2008. Patterned nonadhesive surfaces: superhydrophobicity and wetting regime transitions. Langmuir 24 (4), 1525–1533. https://doi.org/10.1021/la702239w.

Reylon (2024) ⟨https://www.reylon-plasma.com/glossary/polyethylene/?lang=em⟩ (accessed November 2024).

Roach, P., Farrar, D., Perry, C.C., 2005. Interpretation of protein adsorption: surface-induced conformational changes. J. Am. Chem. Soc. 127, 8168–8173. https://doi.org/10.1021/ja042898o.

Rosmaninho, R., Melo, L.F., 2006. Calcium phosphate deposition from simulated milk ultrafiltrate on different stainless steel-based surfaces. Int. Dairy J. 16, 81–87. https://doi.org/10.1016/j.idairyj.2005.01.006.

Saget, M., de Almeida, C.F., Fierro, V., Celzard, A., Delaplace, G., Thomy, V., Coffinier, Y., Jimenez, M., 2021. A critical review on surface modifications mitigating dairy fouling. Compr. Rev. Food Sci. Food Saf. 20 (5), 4324–4366. https://doi.org/10.1111/1541-4337.12794.

Schmidt, R.H., 1997. Basic Elements of Equipment Cleaning and Sanitizing in Food Processing and Handling Operations. FS14, Food Science and Human Nutrition Department, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences. University of Florida (http://edis.ifas.ufl.edu).

Taylor, S.L., Hefle, S.L., Bindslev-Jensen, C., Bock, S.A., Burks Jr, A.W., Christie, L., Hill, D.J., et al., 2002. Factors affecting the determination of threshold doses for allergenic foods: How much is too much. J. Allergy Clin. Immunol. 109 (1), 24–30. https://doi.org/10.1067/mai.2002.120564.

Thyparambil, A. (2015) Development, Validation, And Application Of Analytical Methods For Characterizing Adsorbed Protein Orientation, Conformation, And Bioactivity. All Dissertations. 1512. ⟨https://tigerprints.clemson.edu/all_dissertations/1512⟩.

U.S. Department of Agriculture, 2020 Agricultural Research Service. Peanut buthttps://fdc.nal.usda.gov/food-details/1100559/sourcester - USDA FoodData Central Food Details Accessed November 2024.

van Oss, C.J., Giese, R.F., 1995. The hydrophilicity and hydrophobicity of clay minerals. Clays Clay Miner. 43, 474–477. https://doi.org/10.1346/CCMN.1995.0430411.

van Oss, C.J., Good, R.J., Chaudhury, K., 1988. Additive and Nonadditive Surface Tension Components and the Interpretation of Contact Angles. Langmuir 4, 884–891 doi/10.1021/la00082a018.

Verran, J., Packer, A., Kelly, P., Whitehead, K.A., 2010. The retention of bacteria on hygienic surfaces presenting scratches of microbial dimensions. Lett. Appl. Microbiol. 50, 258–263. https://doi.org/10.1111/j.1472-765X.2009.02784.x.

Whitehead, K.A., Rodgers, D., Colligon, J., Wright, C., Verran, J., 2006. Use of the Atomic Force Microscope to determine the effect of substratum surface topography on the ease of bacterial removal. Colloids Surf. B: Biointerfaces 51, 44–53. https://doi.org/10.1016/j.colsurfb.2006.05.003.

Williams, D.F., Kellar, E.J.C., Jesson, D.A., Watts, J.F., 2017. Surface analysis of 316 stainless steel treated with cold atmospheric plasma. Appl. Surf. Sci. 403, 240–247. https://doi.org/10.1016/j.apsusc.2017.01.150.

Yang, H., Etzel, M.R., 2003. Evaluation of three kinetic equations in models of protein purification using ion-exchange membranes. Ind. Eng. Chem. Res. 42, 890–896. https://doi.org/10.1021/ie020561u.