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Influence of substrate nature and β -lactoglobulin on cleanability after soiling by suspension spraying and drying



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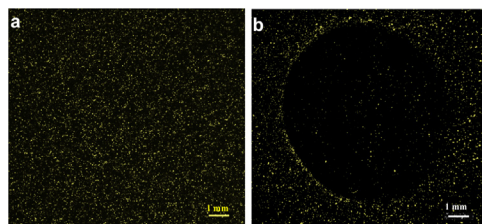
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HIGHLIGHTS

- β -lactoglobulin improves cleanability owing to lowering of surface tension.
- Surface tension is more important than contact angle for capillary forces.
- Protein denaturation has a minor effect on cleanability.
- Organic contaminants coexist with adsorbed protein.
- Organic contaminants complicate the understanding of soil adherence and cleanability.

GRAPHICAL ABSTRACT



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ABSTRACT

Glass and stainless steel (StSteel, AISI304-2R), previously cleaned with ethanol (-Eth) or with ethanol and UV-Ozone treatment (-UVO), were soiled with quartz suspensions in water and in a β -lactoglobulin (β -LGB) solution, and dried. The cleanability (ease of quartz particle detachment) in water was evaluated using a radial-flow cell. The soiling suspension containing β -LGB was used as such or after heating for 4 h at 75 °C, which provoked coagulation of about 75% of β -LGB. The substrate–solution interfaces were characterized by X-ray photoelectron spectroscopy (XPS) analysis of conditioned substrates and by contact angle measurements. The substrate surfaces are covered by a layer of organic contaminants which are not removed by pre-cleaning or are adsorbed from the surroundings. The presence of β -LGB in the soiling suspension leads to protein adsorption, but a significant amount of contaminants remains at the surface.

For three of the substrates tested (Glass-Eth, Glass-UVO, StSteel-UVO) the increase of cleanability when the soiling suspension contained β -LGB may be explained by lower capillary forces acting upon drying. Capillary forces are proportional to the liquid surface tension and depend in a less important way on substrate contact angle. However the order of cleanability observed for the substrates soiled with a suspension of quartz particles in water (Glass-Eth \cong Glass-UVO < StSteel-UVO < StSteel-Eth) and the

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influence of β -LGB on the cleanability of StSteel-Eth may not be explained only by computed capillary forces. The contact angle may exert a direct influence on droplet spreading and particle–substrate contact. The organic contaminants present on the surfaces, which are often neglected by supposing model solid surfaces, may have a significant influence on cleanability through physico-chemical processes which remain to be appreciated.

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1. Introduction

Cleaning is an important process in food and pharmaceutical industries. Its efficiency influences the final quality of the products, and is crucial to insure the absence of cross-contaminations and batch integrity (Stephan et al., 2004). A good control of fouling, accompanied by an effective cleaning process, may contribute to reduced fouling-related cost such as additional energy, productivity loss, additional equipment, manpower, chemicals and environmental impact.

Particle deposition and drying are a mode of fouling which is of major concern for surfaces exposed to natural environments or surfaces of industrial equipment. Particulate soils may originate from splashing on open surfaces or deposition in storage tanks, ducts or heat exchangers. The issue is of particular concern in food processing, in the catering industry or in medical applications where high hygienic levels must be maintained. Compounds present in food and pharmaceutical mixtures may influence interactions with surfaces and adhesion processes (Speranza et al., 2004).

A study of starch granules adherence, after suspension spraying onto different substrates and drying, demonstrated that substrate wettability influenced the shape and compactness of the adhering aggregates, the efficiency of shear forces upon cleaning, and finally the adherence of soiling particles (Detry et al., 2011). Moreover, it was reported that the presence of macromolecules, mainly polysaccharides, which were adsorbed from the liquid phase or carried by the retracting water film and deposited at the granule–substrate interface, acted as an adhesive joint, the properties of which seemed to be influenced by the detailed history of drying and subsequent exposure to humidity.

The influence of macromolecules (Touré et al., 2014a, 2013, 2011) on the adherence of model particulate soils (quartz particles) was examined using substrates which differed according to hydrophobicity. The presence of bovine serum albumin (BSA) had little effect on the particles adherence to a hydrophobic substrate (polystyrene) but decreased drastically their adherence to a more hydrophilic substrate (glass), bringing it to the range observed for polystyrene. There was no significant difference in particle adherence depending on whether BSA was involved by conditioning the substrate before soiling, or by its presence in the soiling suspension, or both ways (Touré et al., 2014a). BSA did adsorb on quartz particles and on glass and polystyrene but its influence on particle adherence to glass was attributed to the lowering of the liquid surface tension, leading to a decrease of capillary forces created during drying. The influence of β -lactoglobulin (β -LGB) on quartz adherence to glass was analogous to that of BSA (Touré et al., 2013). The effect of dextran was weak in accordance with a weak effect on liquid surface tension and with a low adsorption by solids or easy desorption (Touré et al., 2014a, 2011).

Whey proteins are often used to improve food product qualities such as texture and appearance. A controversial question concerns their implication in deposit layer formation and removal. Although the connection between the thermal stability and conformational changes of β -LGB is well established, the role of its denaturation in the build-up of the fouling deposit is still unclear (Blanpain-Avet

et al., 2012; Bansal and Chen, 2006, 2005). Bansal et al. (2005) reported that aggregated whey proteins and dissolved denatured whey protein took part in deposit formation. Although there is no general consensus in the literature (Bansal and Chen, 2006; Changani et al., 1997), according to Robbins et al. (1999) β -LGB plays a key role in fouling as it is the most abundant and the most heat-labile whey protein.

A matter of interest is the influence of heating and protein denaturation on particulate soil adherence. Recently (Touré et al., 2014b), we showed that the presence of β -LGB in a fouling quartz suspension slightly increased the particle adherence to stainless steel pre-cleaned with ethanol, which was further slightly increased when the protein was denatured. Comparison with systems investigated before indicated that stainless steel did not behave as a hydrophilic substrate.

The water contact angle measured on stainless steel is frequently above 40° , much higher than that expected for a surface made of chromium and iron oxy-hydroxides, which are of hydrophilic nature. Actually, inorganic surfaces made of oxides (e.g. stainless steel and glass) or metals (e.g. gold) are characterized by a high surface energy, i.e. an excess of free energy due to a lack of bonds balance at the solid surface. This tends to be reduced by retention of organic compounds which originate from material processing or are contaminants adsorbed from the surroundings. As a result, these surfaces are less hydrophilic than expected (Rouxhet, 2013). It thus appears suitable to consider the influence of the initial state of the surface on its behavior regarding soiling and cleaning.

The aim of the present work is to investigate the effect of β -LGB and its denaturation on the adherence of particulate soils, depending on the nature of the substrate and the state of its surface. The ease of particle detachment, i.e. the substrate cleanability, was evaluated by exposure to water in a radial flow chamber (RFC). Glass and stainless steel were taken as models of practically relevant substrates regarding particulate fouling and cleaning. The influence of the initial surface state was examined in relation with hydrophobicity. Therefore the tested substrates were cleaned in two ways before soiling: solvent rinsing, and UV–Ozone treatment (UVO) which insured a more extensive removal of organic contaminants. Quartz particles were kept as a model of hard particulate soil. The protein was involved in the soiling process by its introduction into the quartz suspension. The influence of denaturation was examined by a high temperature pretreatment of the soiling suspension. In a previous work, we showed that there was no difference in particles detachment, whether the β -LGB denaturation occurred by drying the soiled substrate at high temperature or by previous heating in the quartz suspension (Touré et al., 2014b). In order to possibly relate directly the particles adherence to the properties of the soiling suspension (surface tension, contact angle), the second procedure was used here. The soiling suspension was characterized at different stages regarding soluble protein concentration, conformational changes and surface tension. The interfaces were characterized by X-ray photoelectron spectroscopy (XPS) analysis of substrates conditioned with solutions in representative states and by contact angle measurements.

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