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Real time study of detergent concentration influence on solid fatty acid film removal processes

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Abstract

Cleaning in aqueous solution is a complex mechanism which depends on several parameters. The Quartz Crystal Microbalance (QCM) technique was used to investigate the detachment, using two detergents: GP 17.40 SUP and Galvex SU 99, of stearic acid ($C_{18}H_{36}O_2$) films deposited on gold-coated quartz surfaces. The cleaning mechanism was observed in real time by measuring the frequency of a quartz crystal during the fatty acid film removal. These observations reveal two successive phenomena: firstly, adsorption and absorption of water and detergent on the stearic acid layer and, secondly, the detachment of the fatty acid layer. A relationship between removal time and detergent concentration was highlighted: fatty acid removal time decreases as detergent concentration increases until an asymptotic value is reached. Initial contamination greatly influences cleaning duration. Increased sample contamination actually leads to increased removal time. However, no real correlation between the two parameters can be established. As a result, optimal parameters can be determined for each detergent, thus the QCM technique appears to be of great interest in monitoring and optimizing cleaning protocol.

Keywords: Quartz Crystal Microbalance; detergency process; fatty acid removal; water adsorption; detergent adsorption; stearic acid.

1. Introduction

In aqueous solution, cleaning is governed by several mechanisms based either on detergent adsorption (roll-up and emulsification [1, 2]) or on detergent absorption (solubilisation [3]). The efficiency and the quality of a cleaning process are controlled by many parameters. Some of these are solution temperature [4], detergent concentration [4, 5], ultrasound presence, the soil-detergent pair [3, 6], solution ageing, cleaning duration [4], etc. Moreover, the quality of the process can be evaluated by three criteria which are the physicochemical state of the treated surface (presence of soil or detergent residues), economic cost (time, energy and consumables) and environmental impact. Also, wastewaters resulting from cleaning processes contain various contaminants including detergent which can be toxic to aquatic life [7]. Filtration and ultrafiltration techniques have been developed in order to remove surfactants from wastewater [8, 9], thus the

reduction of detergent concentration in the cleaning processes can simplify wastewater treatment. The ability to measure the influence that experimental parameters (*e.g.* detergent concentration) of the cleaning process have on its efficiency therefore appears to be a promising challenge. The efficiency of removing soil from a surface has been widely studied. Several techniques enabling detection of an organic layer on a surface have been explored: X-Ray Photoelectron Spectroscopy [10, 11], ellipsometry [12, 13], contact angle measurements [14-17], Infra-Red spectroscopy [18, 19], Quartz Crystal Microbalance (QCM) [5, 20, 21], etc. The Quartz Crystal Microbalance (QCM) technique is used to measure changes in masses on a quartz crystal surface. In fact, quartz crystal frequency changes according to its variations (increases or decreases) in mass. The changes in mass for thin and homogeneous film can be estimated with Sauerbrey's equation [22] as follows:

$$\Delta f = -\frac{2f_0^2}{\rho_q \cdot c} \cdot \frac{\Delta m}{A}$$

{1}

Where Δf (in Hz) is the variation in frequency induced by variation in mass Δm (in g), ρ_q represents crystal density ($\rho_q = 2.648 \text{ g cm}^{-3}$). f_0 (in Hz) is the fundamental resonance frequency (Hz) of quartz crystals. c is the velocity of a transversal wave in quartz crystal ($c = 3.34 \cdot 10^5 \text{ cm s}^{-1}$ for an AT-cut quartz crystal). A (in cm^2) is the sensitive area. Application fields for this technique are numerous: monitoring thicknesses in vacuum deposition processes [23], detection of organic vapour [24], study of biological reactions [25] and monitoring the removal of solid organic soils. For this last application, Weerawardena et al.'s works [5, 20, 21] focused on the ability of different non-ionic surfactants to

remove organic soils. Triglycerides (tripalmitin and tristearin) and alkane (dotriacontane) were used as soils. As a result, surfactants were classified according to the percentage of soil remaining on the surface.

In this paper we examine layers of stearic acid ($C_{18}H_{36}O_2$) deposited by spin coating on gold-coated quartz surfaces in order to simulate organic pollution. Stearic acid was chosen since it is included in the composition of polishing and wax pastes [26] used for jewellery. After polishing, residual stearic acid may remain on surfaces. The influence of the detergent concentration and the mass deposited on stearic acid removal duration was studied. The different steps of the removal process were followed *in situ* by the QCM technique. In order to know the amount of residue remaining on the quartz surface, the sample was rinsed and dried and its frequency measured. The cleaning test is considered valid if more than 90% of the stearic acid is removed, a percentage calculated by measuring quartz frequency after each experiment. The time necessary to reach this degree of removal is the defining criterion of cleaning efficiency.

Although the QCM technique has been used previously to study the removal of solid organic film, only the percentage of residual contamination was investigated. This paper presents the first use of the QCM technique to assess the influence on cleaning processes of both detergent nature and concentration.

2. Experimental Procedures

2.1. Materials

Stearic acid, more than 99% pure, was purchased from Fischer Bioblock Scientific. Polluting solutions were prepared by dissolving the acid in HPLC-grade Tetrahydrofuran (THF).

The QCM, the AT-cut quartz crystals and the flow cell were provided by Testbourne Ltd. (England). The fundamental resonance frequency of quartz crystals is 5 MHz, with a diameter of 1-inch, and a thickness of 330 μm . The sensitive areas are the gold electrodes (approximately 250 nm thick) located on both sides of the quartz, deposited on a chrome under-layer (approximately 10 nm thick). The electrode on which the stearic acid is deposited is $\frac{1}{2}$ inch in diameter, the other electrode $\frac{1}{4}$ inch. Their surface area (approximately $0.05 \text{ in}^2 \approx 0.32 \text{ cm}^2$) constitutes the sensitive area (*i.e.* where the electrodes overlap) during the frequency measurements. The electrodes are designed to be smaller than the entire quartz so as to limit the mechanical stress created by the crystal holder. Side effects are avoided thanks to the difference in area of the two electrodes.

Two detergents were used: GP 17.40 SUP and Galvex SU 99 from NGL Cleaning Technologies (Switzerland). Both are used to clean and meticulously prepare surfaces for applications such as vacuum deposition, biomedical implant cleaning, etc. These detergents are formulated with several surfactants (ionic and non-ionic surfactants) and alkali metal salts.

2.2. Sample preparation

The quartzes were cleaned for 4 minutes in an ultrasonic bath containing alkaline detergent GP 17.40 SUP (10 g L^{-1} , 60°C). They were then rinsed in successive baths of tap and demineralised water and dried by spinning.

The influence of two parameters on cleaning time was studied: detergent concentration and initial contamination. For the former, all the samples were contaminated with a $9.0 \pm 0.5 \mu\text{g cm}^{-2}$ stearic acid layer deposited by spin coating. For the latter, three solutions of stearic acid in THF were used (6 g L^{-1} , 12 g L^{-1} and 18 g L^{-1}). By varying rotation speeds between 1000 and 3000 rpm, layers from 4.5

$\mu\text{g cm}^{-2}$ to $16 \mu\text{g cm}^{-2}$ can be achieved. The deposited mass of stearic acid was measured using the QCM technique. The polluted quartzes were kept at 20°C for a 24-hour period before use. After evaporation of THF, the stearic acid films on the quartz surface are solid.

2.3. Stearic acid removal

400 mL of demineralised water with detergent at the desired concentration was prepared for each test. The experiment setup is comprised of a 100 mL flow cell in which the quartz is mounted and of a closed circuit where the detergent solution is circulated by a centrifugal pump. With this configuration, the flow rate measured is $840 \pm 40 \text{ mL min}^{-1}$. Resonator frequency was measured in real time. The typical shape of frequency versus time is shown in Figure 1.

From t_0 to t_1 the quartz is in air. Its polluted surface then comes in contact with the liquid flow cell. With the quartz immersed in liquid, frequency suddenly decreases. Between t_1 and t_2 , adsorption and absorption phenomena cause a further decrease in frequency, which is due to an increase in the quartz mass. This phenomenon of water and surfactant adsorption has been previously shown by Weerawardena et al., using the QCM method [20] and by Bäckström et al. using *in situ* ellipsometry measurement [27].

After t_2 , removal mechanisms become predominant, until t_M when maximum removal is reached. After t_M the frequency remains constant which means that there was no further decrease in mass, and the test thus ends. After the cleaning cycle the quartz was rinsed with both tap and demineralised water and then dried. A new frequency measurement indicates the residual mass. The test is considered as valid if more than 90% of the stearic acid deposit has been removed. If so,

cleaning time – t_{clean} – can be calculated as follows: $t_{\text{clean}} = t_M - t_I$. This will be our efficiency parameter of the detergency process.

3. Results and discussion

3.1. Preliminary tests

Before beginning the tests, two points must be investigated. Firstly, the impact of rinsing and drying the quartz on its frequency was studied. Secondly, preliminary tests were conducted in order to choose initial temperature conditions, taking into account that this parameter has a great impact on cleaning speed. Rinsing and drying the samples are also critical aspects of the cleaning process. In order to study the impact on frequency changes, experiments on clean quartz were undertaken. In one case, tests were conducted with no detergent. In another case, the concentration of GP 17.40 SUP was set at 10 g L^{-1} . In both cases, the temperature was $20^\circ\text{C} \pm 1^\circ\text{C}$. The experiments were stopped after 10 minutes. After rinsing and drying, frequency was measured. A variation up to $\pm 10\text{ Hz}$ in comparison to the pre-test frequency measurement was found, corresponding to a mass of $\pm 0.2\text{ }\mu\text{g cm}^{-2}$, smaller than the tolerated residual stearic acid masses. To determine temperature conditions, solutions of GP 17.40 SUP at 25 g L^{-1} , and Galvex SU 99 at 50 g L^{-1} were first used at $20 \pm 1^\circ\text{C}$. These concentrations were chosen in accordance with the manufacturer’s advice. t_{clean} was 2 minutes for GP 17.40 SUP and 18 minutes for Galvex SU 99. This preliminary test showed that the process was not adapted for Galvex SU 99. The temperature was thus raised to 35°C for this detergent in order to work with shorter t_{clean} , as increasing the temperature improves detergent efficiency [28, 29]. With this new parameter, t_{clean} fell to 3 minutes 30 seconds at 50 g L^{-1} , thus enabling us to set the environmental

conditions (e.g. the temperature) in order to investigate the influence of detergent concentration and pollution mass.

3.2. Detergent concentration versus cleaning time

The evolution of stearic acid removal time as a function of detergent concentration, shown in Figure 2, is similar for GP 17.40 SUP and Galvex SU 99. For both detergents, cleaning time is actually very long at low concentrations (e.g. more than 15 minutes at 2.5 g L^{-1}) and decreases abruptly to reach an asymptotic value corresponding to the critical concentration from which t_{clean} remains constant. Thus, above this critical concentration, it may be necessary to change other parameters – such as temperature – to decrease t_{clean} , reckoning that surfactant concentration no longer has any influence. According to Figure 2, critical concentrations are estimated at 12.5 g L^{-1} and 20 g L^{-1} respectively for both GP 17.40 SUP and Galvex SU 99. Above these values, t_{clean} stagnates at 118 ± 16 seconds for the first detergent and 236 ± 25 seconds for the second. As the critical micelle concentration cannot be defined for detergents formulated with several surfactants, the critical concentration introduced here appears to be a useful parameter of cleaning protocol efficiency. In order to explain the vertical asymptotical behaviour of t_{clean} when the concentration tends to zero (Figure 2), an experiment was conducted with no detergent. Figure 3 shows the change in mass on a polluted quartz surface in demineralised water. It must be noted that stearic acid cannot be removed by water only, even if heated to 35°C . Moreover, comparison of a polluted quartz to a clean one indicates that water adsorption and infiltration occurred on the stearic acid layer. In fact, frequency decreases abruptly for the clean quartz (due to the air/liquid transition), remaining constant after 1 minute, whereas it takes more than 50 minutes to observe frequency stagnation for

the polluted one. This stagnation results of water saturation on the stearic acid layer. As frequency did not increase, the removal mechanism did not take place. Once the quartz is dry, frequency measurement indicates that the entire stearic layer remains on the quartz surface. This result is in accordance with the exponential behaviour shown in Figure 2: when detergent concentration tends to zero, t_M and consequently t_{clean} tends to infinity. This adsorption and absorption of water and detergents provided by the cleaning solution in the stearic acid film governs the first step of the cleaning process. It can be studied using the QCM technique by plotting $t_{sorption}$ (see Figure 1 for the definition), water adsorption or absorption time, as a function of concentration. Figure 4 shows this evolution for GP 17.40 SUP to have a similar shape to t_{clean} as a function of concentration (Figure 2): rapid decrease and stagnation above the same critical concentration value of 12.5 g L^{-1} . Below the critical concentration, the more concentrated the cleaning solution, the faster the polluted quartz surface will load the detergent. Above the critical concentration, $t_{sorption}$ is very short: 2.5 ± 0.5 seconds, meaning that sufficient surfactants have been absorbed to infiltrate the stearic acid film and saturate it. The concordance between the evolution of t_{clean} and $t_{sorption}$ as a function of detergent concentration may imply that the sorption phenomenon governs the cleaning process.

3.3. Initial contamination versus cleaning time

Another parameter which may have notable influence on cleaning is the initial contamination of the quartz surface (i.e. the mass of stearic acid deposited on the surface). In order to study this influence, experiments were conducted with contamination masses ranging from $4.5 \text{ } \mu\text{g cm}^{-2}$ to $16 \text{ } \mu\text{g cm}^{-2}$. Figures 5a and 5b show cleaning time evolution versus initial contamination for GP 17.40 SUP and

Galvex SU 99. As expected, cleaning time increases with initial contamination for both detergents, whatever their concentrations. For example, for GP 17.40 SUP at 10 g L^{-1} , t_{clean} varies from 120 seconds for an initial contamination of $4.7\text{ }\mu\text{g cm}^{-2}$ to 374 seconds for $15.6\text{ }\mu\text{g cm}^{-2}$. For the tests conducted with Galvex SU 99, the two concentrations chosen (20 g L^{-1} and 50 g L^{-1}) are equal to or above the critical concentration. The two sets of data in Figure 5b nearly merge for the contamination range under study, indicating that t_{clean} is the same for the two detergent concentrations. Although the critical concentration has been defined for an initial contamination of $9.0 \pm 0.5\text{ }\mu\text{g cm}^{-2}$, this value appears to be valid for a lower contamination (half the initial one) and also for a higher contamination of stearic acid (twice as much). Apart from these results, no real correlation could be established between initial contamination by stearic acid and t_{clean} .

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Authors Biographies

Olivier Favrat received a master degree in mechanical engineering (1999) at the Top School ENSMM, France in 2006 and a Ph.D. in engineering science from the University of Franche-Comté, France in 2011. His research-interests include physico-chemical characterization of surfaces.

Joseph Gavaille received a Ph.D. in engineering science from the University of Franche-Comté (France, 2002). In 2006 he was nominated as Assistant Professor in materials science at the Top School ENSMM, France. His studies are focused on the mechanical and physico-chemical properties of surfaces.

Lotfi Aleya is currently senior Professor at the National Centre for Scientific Research (CNRS 6249, Besançon, France). He pilots cooperative research projects in France and other countries associated with his Chair. Among his research topics, he studied the cleaning processes coupled to aquatic life status.

Guy Monteil is currently Professor at the Top School ENSMM, France and director of the Applied Mechanics Department of the FEMTO-ST Institute (France). His research-interests include surfaces micro-analysis.

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Fig. 1 General shape of the frequency changes during cleaning process. Resonator is in air from t_0 to t_1 . The cleaning process begins and can be divided into two steps. First, from t_1 to t_2 (ie t_{sorption}), the surface resonator is loaded through adsorption and infiltrated with detergent and water on the polluted surface. Then, from t_2 to t_M , the soil is removed and the resonator is unloaded. Total cleaning time is $t_{\text{clean}} = t_M - t_1$

Fig. 2 t_{clean} as a function of concentration for two detergents (GP 17.40 SUP at $20 \pm 1^\circ\text{C}$ and GALVEX SU 99 at $35 \pm 1^\circ\text{C}$). Samples have been polluted by stearic acid with masses of $9 \pm 0.5 \mu\text{g.cm}^{-2}$

Fig. 3 Influence of pollution on frequency as a function of time in demineralised water at 35°C . The decrease in frequency in the case of polluted samples means that adsorption and absorption occur but stearic acid is not removed. The clean quartz shows that little adsorption or absorption take place

Fig. 4 Time of adsorption and absorption of water and detergent (GP 17.40 SUP at $20 \pm 1^\circ\text{C}$) versus concentration. Samples have been polluted by stearic acid with masses of $9 \pm 0.5 \mu\text{g.cm}^{-2}$

Fig. 5 t_{clean} as a function of initial contamination for two detergents (a): GP 17.40 SUP at $20 \pm 1^\circ\text{C}$ and (b): GALVEX SU 99 at $35 \pm 1^\circ\text{C}$

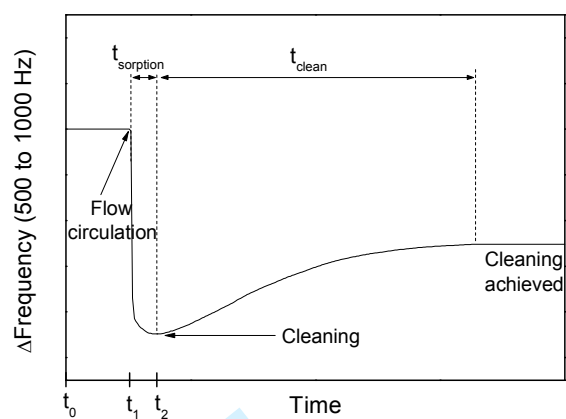


Fig. 1

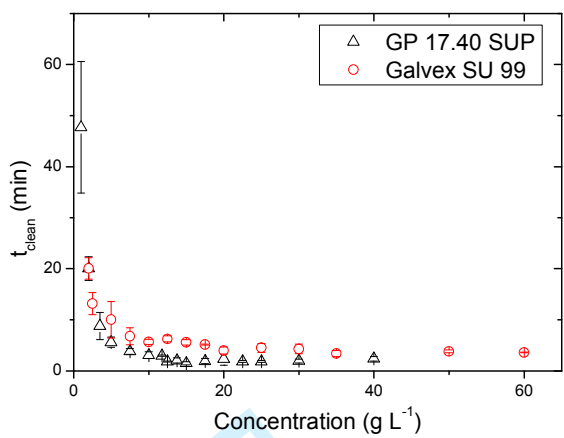


Fig. 2

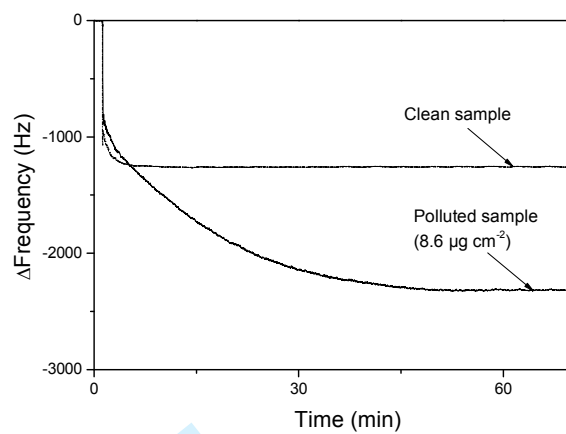


Fig. 3

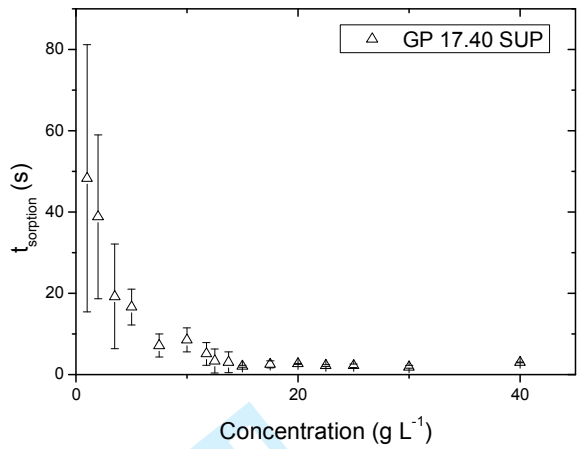


Fig. 4

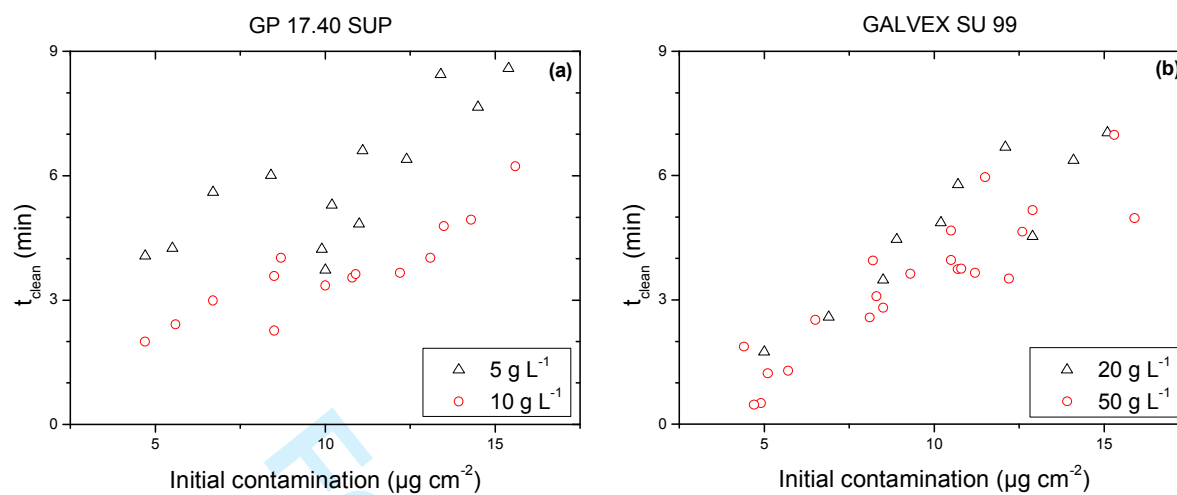


Fig. 5