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OBSERVATION OF THE CLOGGING OF PDMS MICRO-SEPARATORS BY MICROMETRIC PARTICLES

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KEY WORDS

filtration, fouling, particle capture, separation, microchannel, membrane, colloid, pore blockage

ABSTRACT

In this paper, we report experiments where the capture of micron-sized particles is observed in a poly-dimethylsiloxane (PDMS) microfluidic device. The filtering part of the device consists of an array of parallel micro-channels (width: 20 microns, height: 50 microns). Direct observations of the filtering part by video-microscopy allow to investigate the way the fouling of the microchannels by the particles is taking place. The experimental results underline the important role played by the PDMS "conditioning" on the way particles are captured during filtration. When a filtration experiment is performed after a rinse of the PDMS microsystem with ultrapure water, the particles first form arches at the microchannels entrance, then leading to the growth of a filtration cake. When a filtration experiment is performed after a rinse with a saline solution (water with KCl at 10^{-1} M), the particles are captured on the walls between the microchannels, then leading to the progressive formation of dendrites. As the experiments are performed at a constant flow rate, an increase in the pressure drop across the microsystem is observed because of clogging. The formation of dendrites induces a smaller increase in pressure than the formation of a cake. An elution of the PDMS with the saline solution may be the reason why these different fouling behaviors are observed.

1. INTRODUCTION

The separation of micron-sized particles from a liquid using a filter is an important operation in numerous industrial processes (with environmental, chemical, pharmaceutical or biomedical applications). This separation can be achieved by different means, for instance: deep-bed filtration, pressure-driven membrane filtration or liquid chromatography. All these processes rely on the capture of particles within a porous medium (deep filtration) or at its surface (screen filtration). Particle capture is sometimes desired (size exclusion in liquid chromatography), but in some cases it appears as a serious limitation of the process (fouling in membrane technology). Furthermore, the understanding of the way particles adhere to the surface and then the reversibility of the capture process (by a phase change, a back-flush ...) is also an important scientific challenge. However, the mechanisms leading to particle capture (and/or detachment) in screen filtration and deep filtration are not yet fully well understood, mainly because of the complex interplay between the hydrodynamic and physico-chemical interactions between the particles and the collecting surface. Macroscopic models have been developed assuming basic mechanisms such as pore clogging, pore section narrowing or cake build-up [1]. These models have been widely used for the description of the flux decline in filtration but it has been often reported that, although they appear to be robust, they lack of significance when particle size distribution, pore size distribution or collective mechanisms have to be

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considered [2]. To progress in the understanding of particle capture by a porous medium, the development of novel, non-invasive, in situ methods for local quantification is a key point [3].

The main objective of this work is to progress in the understanding of the mechanisms leading to particle capture (and/or detachment), in a filter with a well defined pore geometry. In this study, we report direct observations of particles capture and subsequent clogging of a PDMS microfluidic device, thereafter called "micro-separator", mimicking the behavior of a typical filtration unit. As far as the present results are concerned, the micro-separator filtering part consisted of an array of parallel microchannels and experiments were performed in a dead end filtration mode (the direction of the suspension flow is perpendicular to the filtering part).

2. BACKGROUND

Several recent experimental studies based on the use of microfluidic devices have been performed to visualize the clogging phenomenon and/or the formation of the first layers of fouling particles, in order to study particle capture by a porous medium.

Some of these studies relied on the use of microsieve membranes, which consist of thin silicon screens with patterned circular holes. The fabrication of such membranes has been made possible by the recent progresses of micro-engineered membrane technology [4]. Brans et al. [5] observed particle capture on a microsieve membrane [6], using microscopy or confocal scanning laser microscopy. Direct observations of the membrane top surface allowed to make a distinction between the behavior of the small particles (1 micrometers), that deposited at the pore edges and inside the pores, and the behavior of the larger particles (10 micrometers), that deposited exactly onto the pore. By a statistical analysis of the particle deposition locations around the pores of a microsieve, Lin et al. [7] have shown that particles are preferentially captured at two positions: a first one close to the pore edge and a second one located one particle radius further away from the pore center, compared to the first one.

Microfluidics systems made of PDMS have also been used to develop micro-separators, typically consisting in a single wide channel followed by an array of parallel, narrow channels which acts as a filter. These microfluidic devices permit to have a "side view" of the pores, which is complementary from the top view obtained in the aforementioned experiments involving microsieves. They have been used to filtrate latex particles in a dead-end filtration mode [8] or red blood cells in a cross-flow mode [9, 10]. In dead-end mode, Wyss et al. [8] measured the blockage times of the microfluidic channels in order to determine the physical processes governing single-pore clogging. Groisman et al. [9] and Chen et al. [10] designed micro-separators working in a cross-flow filtration mode for the separation of plasma from whole human blood by size exclusion, a potential application being the development of microanalysis system for point-of-care diagnostics. The performance of such devices was seen to be substantially improved with pulsatile pressure (back-pulsing) [9] and by increasing cross-flow velocity [10], similarly to the means usually used to increase efficiency in macroscale cross-flow filters.

3. MATERIALS AND METHODS

The present experiments have been realized with PDMS devices having the same characteristics as those presented in [8]. They allowed to perform filtration of latex particles in a dead-end mode, with a constant flow rate. Direct observation, by digital video microscopy, of particles accumulation at the entrance or inside the micro-channels was made possible by the use of PDMS, which is transparent. Particle capture depended on the microchannels geometry (width and length) and on the hydrodynamic and physico-chemical conditions. Quantitative pieces of information such as, for instance, the amount of particles captured at the filter surface, or the particle trajectories, could be obtained by image processing.

3.1. PDMS micro-separator fabrication and characteristics

The PDMS micro-separators used in the present study were made by the usual soft lithography technique [11]. A sketch of the PDMS micro-separators is shown in Figure 1. The depth of all the channels of the

network was 50 µm. The filtering part of the device consisted of a parallel arrangement of 27 micro-channels. Each microchannel had a set of constrictions along its length such that the smallest width was 20 µm, see Figure 1. The distance between the centres of two successive microchannels was 68 µm. The divergent shape of the main single channel, up the microchannels, was designed to ensure an homogeneous flow of the suspension, over the width of the filtering part.

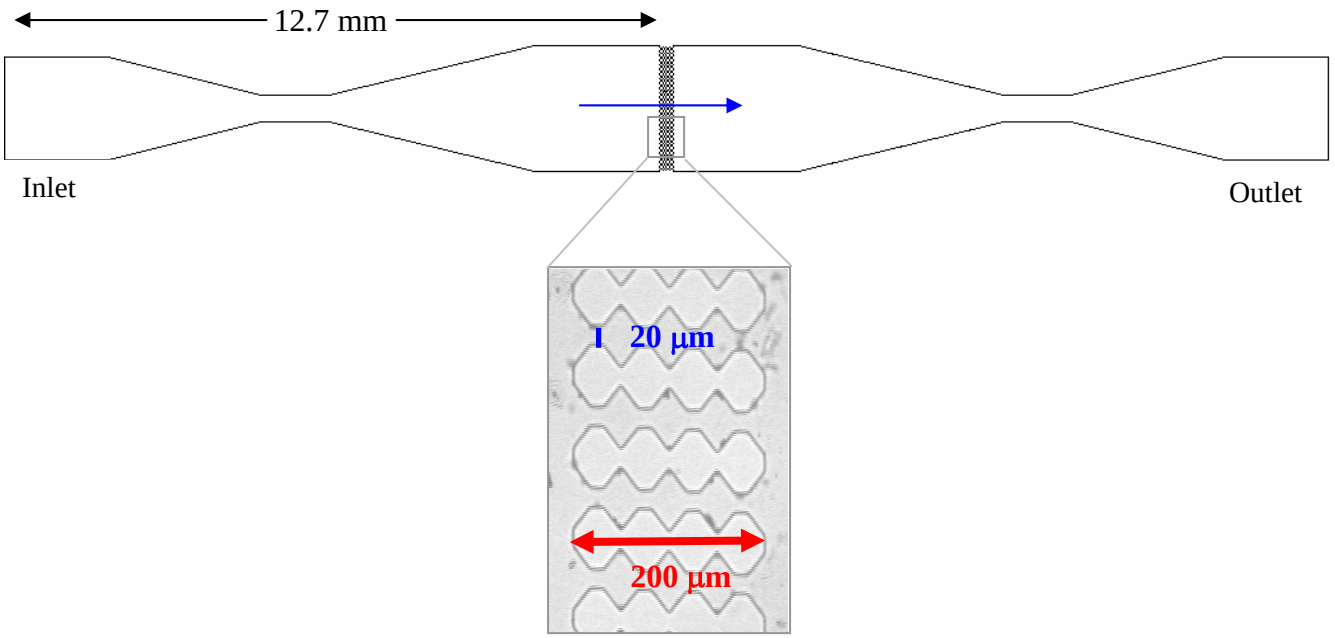

Figure 1: Sketch of the PDMS micro-separators (top) with an image centered on some of the microchannels (bottom). The whole filtering part of the device consisted of a parallel arrangement of 27 microchannels.

3.2. PDMS "conditioning "

The PDMS micro-separators were first cleaned with a Hellmanex solution diluted at 1/1000. Before filtration, the micro-separator was rinsed with a 10^{-1} M KCl solution or with ultrapure water. It will be shown in section 4.2 that this rinse (named "conditioning" step in the next sections affected drastically the way particles were captured during the present filtration experiments.

3.3. Latex suspensions

The suspensions used in the present study consisted in monomodal polystyrene microspheres (latex) dispersed in water. Surfactant-free concentrated particles suspensions were purchased from Invitrogen. The latex particles diameter was 4.9 +/- 0.21 µm. The latex particles were negatively charged with functional sulfate groups on the surface: the zeta potential of the particles, measured with a Malvern Zetasizer, was -57 +/- 5 mV at pH 7.

The latex suspensions used in the filtration experiments were obtained by diluting the concentrated latex suspension in a KCl aqueous suspension until the volume fraction was 10^{-3}. The KCl concentration was varied in the range 10^{-5} M - 10^{-1} M which allowed to modify the suspension stability by changing the magnitude of the repulsive electrostatic interaction between the particles. These concentrations in salt were inferior to the critical concentration for coagulation which was observed by sedimentation tests to be above $2\ 10^{-1}$ M. Prior to experiments, the latex suspensions were observed under microscope to check for the absence of aggregates. Note that such salinity changes also possibly affected the interaction between the particles and the micro-separator PDMS surface.

3.4. Filtration and visualization procedure

In the dead-end filtration configuration used in the present study, a constant suspension flow rate (q = 2ml/h) was imposed through the micro-separators by a syringe pump (Sky Electronic PS 2000). The pressure at the micro-separator inlet (also representative of the pressure drop through the micro-separator) was measured with a pressure sensor (PR41, Keller). The micro-separator was placed on the stage of an Axiolab (Zeiss) microscope, see Figure 2, and images were acquired using a high sensitivity camera (Pixelfly QE, PCO). The dynamic of the micro-channels clogging, at the single pore scale could then be studied using the recorded images. The captured particles positions (for the very first layers of particles to deposit) and, later on, the cake of deposited particles were easily discernible on the images. The exposure time for the camera was 6 ms. As a particle displacement during the exposure time was several times its diameter, the resulting blur could be used to appreciate trajectories of individual particles near the entrance of the microchannels.

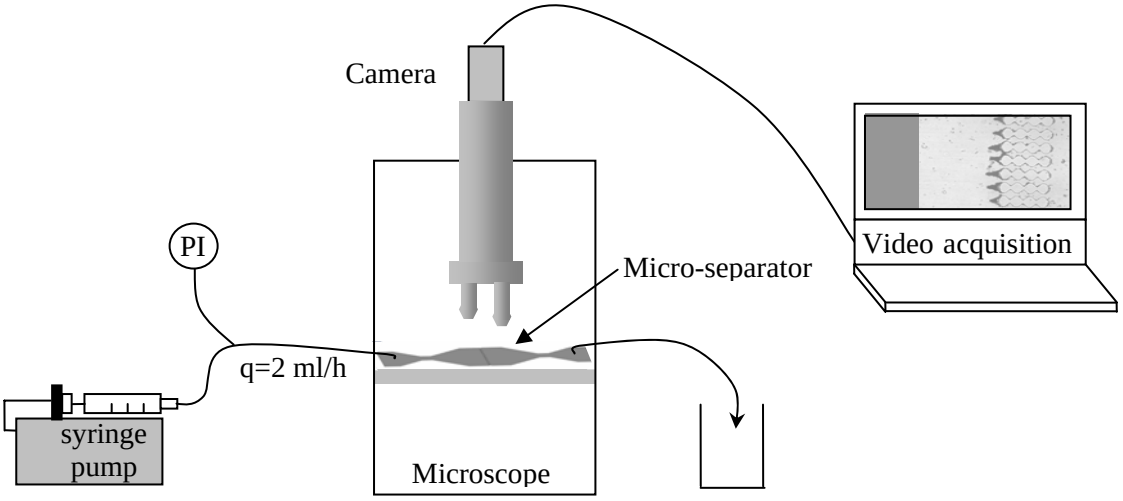

Figure 2: Sketch of the experimental set-up.

4. RESULTS

The results presented in this paper correspond to a technologically important regime in solid/liquid filtration or microfiltration processes, i.e. filtration of a dilute suspension (volume fraction = 0.001) at a high imposed flow rate (q = 2ml/h, i.e. 16.2 m^3/h per square meter of "filter"). For this given flow rate, the Reynolds number for the flow in the large upstream channel was $\mathrm{Re} = U\, d_H / \nu_f = 0.44$, where d_H is the hydraulic diameter, U the typical velocity (U=4.5 mm/s) and ν_f the fluid kinematic viscosity. The Reynolds number for the flow in a single microchannel was 0.58 (typical velocity: 20.5 mm/s). Particle sedimentation could be neglected as the particle settling time (the settling velocity is O(1) μm/s) over the height of the microchannel (50 μm) was much larger than the particle residence time in a microchannel (10 ms).

Inertial effects, which would make the particles deviate from the fluid streamlines when the latter bend close to a microchannel entrance, can be quantified by a Stokes number which is the ratio of the particle viscous relaxation time, $\tau_v = 2a^2 \rho_P / 9\mu_F$, to a typical time scale for the flow through the orifice, $\tau_f = d_p / U$, where d_p is a characteristic microchannel dimension. Using the estimate obtained above for the fluid velocity, U=20.5 mm/s, and taking d_p = 20 μm, it is found that the Stokes number, for the present experiments, are in the range $O(10^{-5}$-$10^{-3})$ so that inertial effects can be neglected.

The effect of Brownian diffusion can be evaluated by the ratio of a typical timescale for the Brownian diffusion of the particles towards the pore edge, τ_d, to the time scale for the flow through the orifice, τ_f. Here, $\tau_d = {d_p}^2 / D_B$, where D_B is the Brownian diffusivity coefficient given by the Stokes-Einstein formula $D_B = k_B T / 6\pi\mu_f a$ (where k_b is the Boltzmann constant). The Péclet number thus obtained, $Pe = \tau_f / \tau_d$, are very large, $O(10^5$ -$10^6)$, so that Brownian motion effects can be neglected as well.

4.1. Influence of particles stability on clogging

As already mentioned, filtration experiments have been performed for various KCl concentrations. The salt concentration had an important effect on the capture rate. No particle capture was observed when the KCl concentration was below 10^{-2} M. Particle capture became observable at 10^{-2} M (few particles were captured on the micro-separator walls) and was relatively important at 10^{-1} M (particles clogging was significant). These results show that the suspension stability had an important effect on particle capture: when the salt concentration increased, the repulsive electrostatic interaction between the particles was reduced, which promoted particle-particle adhesion. Note that it also possibly changed the interaction between the particles and the micro-channels PDMS walls. As already mentioned in studies on particle deposition [12] these interaction have an important effect on particle capture. Experimental results presented in the next subsection were obtained with a KCl concentration of 10^{-1} M, in order to reach significant particle capture rates during the experiments.

4.2. Influence of PDMS conditioning on the clogging

The micro-separator clogging was found to be highly sensitive to the conditioning step of the micro-separator (see section 3.2). Figures 3 and 4 show the progressive development of the micro-separator clogging, for the 10^{-1} M KCl conditioning and for the ultrapure water conditioning, respectively.

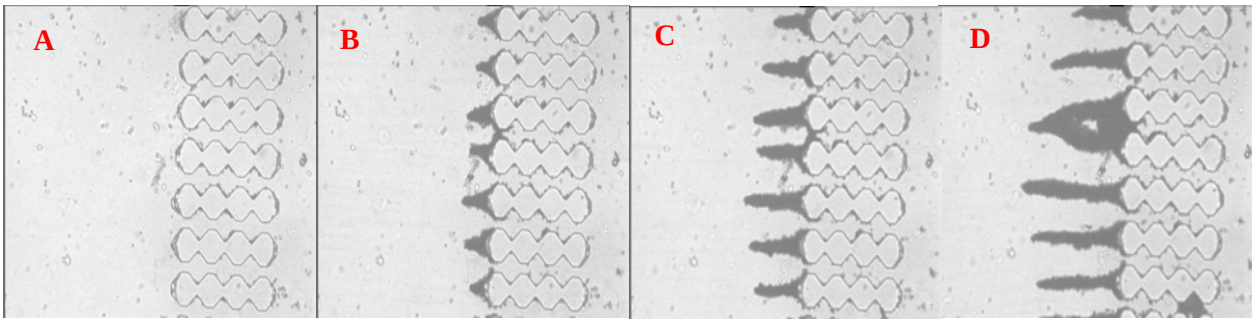

Figure 3: Observation of particle capture after a conditioning of the micro-separator with a KCl solution, leading to the formation of dendrites. Image A was taken at t_0 + 1min (at t_0, the suspension starts flowing into the microchannels), image B at t_0 + 20 min, image C at t_0 + 45 min and image D at t_0 + 90 min.

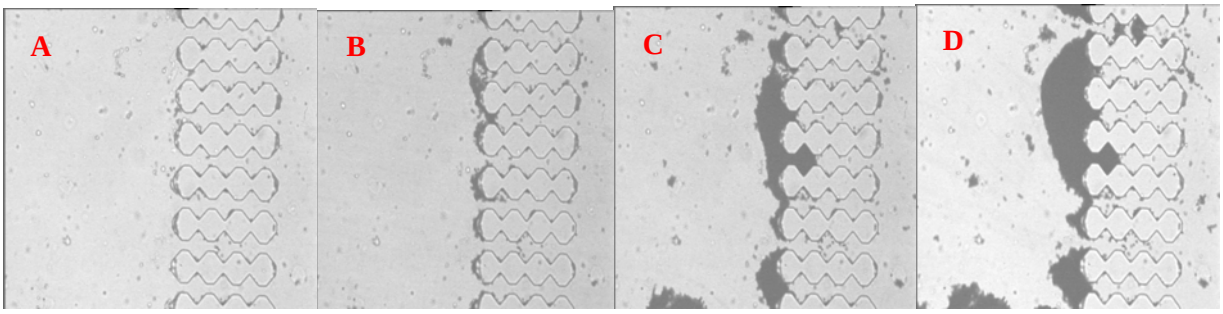

Figure 4: Observation of particle capture after a conditioning of the micro-separator with ultrapure water, leading to the progressive obstruction of the microchannels, and then formation of a filtration cake. Image A at t_0 + 1min, image B at t_0 + 20 min, image C at t_0 + 45 min and image D at t_0 + 90 min.

It is clearly seen that particle capture within the micro-separator was not occurring the same way for the two different conditioning steps. For a conditioning with a KCl solution (Figure 3), particle capture led to the formation of dendrite on the PDMS surface between the microchannels. After 90 minutes of filtration, the

length of these dendrites could reach more than 200 µm, i.e. 40 particle diameters. For a conditioning of PDMS with ultrapure water (Figure 4), particle capture led to a progressive obstruction of the microchannels, provoking the progressive and continuous growth of a filtration cake. The cake formation was not homogeneous on the micro-separator: during a while, some channels could stay open whereas others were already completely clogged.

From a detailed visual inspection of the recorded images, it could be deduced that the clogging of the microchannels, as observed in Figure 4, was induced by the fact that particles first formed arches at the microchannels entrance (see Figure 5b). These arches led to pore blocking, which in turn led to the formation of a compact filtration cake. On the contrary, when dendrites were formed (Figure 3), there was no capture of particles at the microchannel entrance (i.e. in the region highlighted by a circle on Figure 5a). Then, arch formation and the subsequent clogging did not happen.

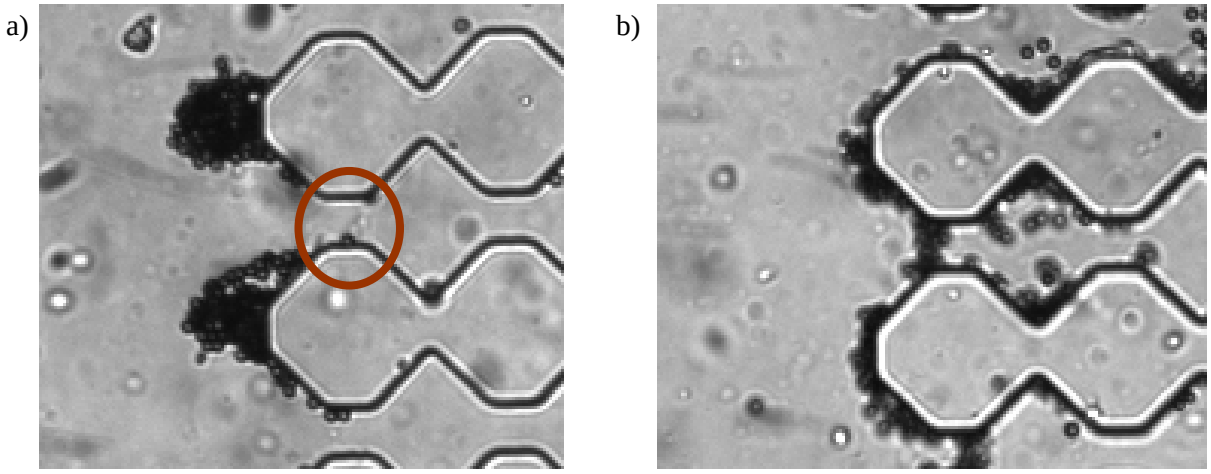

Figure 5: Observation of the first stages of the particle capture. a) after a PDMS conditioning with a KCl solution (image taken 1 min after the beginning of the filtration experiment) , b) after a PDMS conditioning with ultrapure water (image taken 30 s after the beginning of the filtration experiment). The formation of arches at the entrance of microchannels is clearly seen in image b), whereas such a capture is not seen in a).

4.3. Clogging consequences in term of pressure drop

As the present filtration experiments were performed at a constant flow rate, the clogging of the micro-separator resulted in an increase of the pressure drop. Figure 6 shows the evolution of the pressure drop for two experiments performed with the two different PDMS conditioning procedures.

As might have been expected from Figures 3 and 4, the pore clogging following an ultrapure water conditioning caused a more important pressure increase compared to the pore clogging following the KCL conditioning, which resulted in dendrites formation (Figure 3). These results highlight the impact of the particle capture mechanisms (leading either to dendrites or pore blocking) on the hydraulic resistance of the micro-separator and thus on the efficiency of the filtration operation performed.

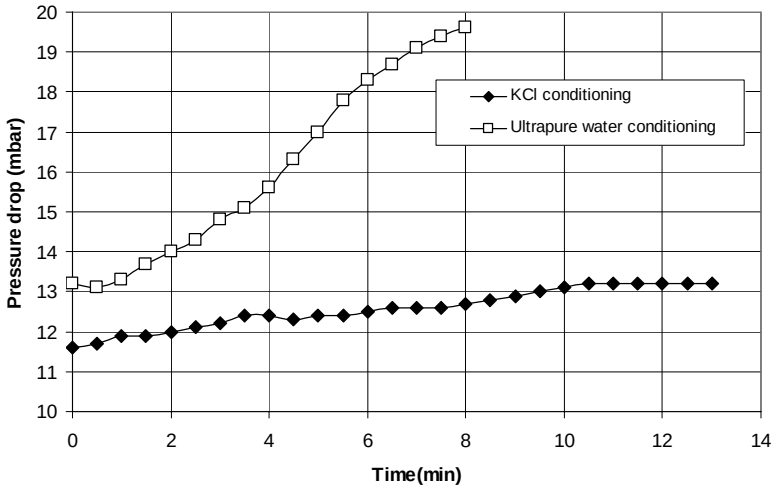

Figure 6: Time evolution of the micro-separator pressure drop for two filtration experiments. Diamonds: experiment performed after a PDMS conditioning with a saline solution. Squares: experiment performed after a PDMS conditioning with ultrapure water.

5. DISCUSSION

The conditioning of PDMS micro-separator with ultrapure water or a saline solution is seen to have an important effect on the way particle capture takes place during filtration experiments performed after the conditioning step. The two different particle capture regimes could be explained by a difference in collision efficiencies on the PDMS wall at the microchannels entrance. It has been observed that dendrites were preferentially formed when no particles were captured in the zone encircled on figure 5a, which corresponded to the bottleneck of the microchannels. On the contrary, the formation of arches could be promoted by efficient lateral collisions between particles and the wall, on the bottleneck zone.

Concerning this latter mechanism, it has been shown [13], using experimental data of observation for particle flow in microtubes (100 μm in diameter), that microtube blockage by arches formation is more likely to occur when the particle to tube diameter ratios is approximately 0.3–0.4, even for low volume fraction (0.005 in [13]). The experimental conditions of the present experiments, with a particle to microchannel width ratio of 0.25 and for volume fraction of 0.001, were therefore close to the ones for which particle arching is likely to occur, according to [13]. These arches led to a progressive clogging of microchannels and then to a quick growth of the deposit on the surface. Dendrites formation should then be favored when there are no efficient lateral collisions between the flowing particles and the bottleneck wall, so that particles arching is not likely to occur.

To our knowledge, there is no publications that study the changes in the physico-chemical properties of PDMS caused by a contact between PDMS and water containing a salt which could help to interpret the present results. However, it could be supposed (at the light of the role played by salt solution in the elution of chromatography support) that the conditioning of the PDMS micro-separator with a saline solution could induce an elution of macromolecules which would be present in the system because of the PDMS fabrication process (uncross-linked of PDMS oligomers) or because of an unwanted contamination (from the Hellmanex solution or other molecules present in water). Such an assumption can be supported by the fact that the conditions for dendrites formation could not be reproduced with freshly prepared PDMS support. Actually, a newly prepared micro-separator had to be rinsed for a long time with salted water before dendrites formation could be observed in a filtration experiment using this micro-separator. The uncross-linked PDMS oligomers have been shown [14] responsible of long tem change (time-scale of days) from hydrophilic surface (after plasma activation) to hydrophobic surface (after a surface rearrangement that bring new hydrophobic groups to the PDMS surface). The extraction of these PDMS contaminants from the bulk polymer with solvents leads to have hydrophilic surfaces that slowly regenerate into hydrophobic surfaces [14]. Klammer et al. [15] have shown that the PDMS requires a pre-conditioning in alkaline solution for 5-6 days before starting biocatalytic reactions. The conditioning of the PDMS with saline solution could play a role in some of these surface modifications. Work to infirm or confirm these assumptions are currently in progress.

6. CONCLUSIONS

The use of PDMS micro-separators allowed filtration experiments to be performed in a filter with a well-defined geometry and controlled hydrodynamic and physico-chemical conditions. Two different modes of particles capture have been evidenced in our filtration experiments depending on a conditioning step of the PDMS device: a rinse prior to the filtration experiment, realized either with ultrapure water or with salted water. The clogging mode occurring when conditioning is performed with ultrapure water has important consequences on the efficiency of the separation: particles arches form at the microchannel entrance, thus leading to a fast and complete fouling of the microchannels. On the contrary, the dendrites that appear when the PDMS is conditioned with a saline solution offer a much lower resistance to the flow. Also, this clogging mode in much less efficient in term of particle capture as particles can still flow through the filtering part of the micro-separator, even when long dendrites have developed. The formation of dendrites seems to be favored when there are no efficient lateral collisions between the flowing particles and the wall at the microchannel entrance. These results are discussed from a possible elution phenomenon of uncross-linked PDMS oligomers with the saline solution. The present study illustrates how the balance between particle transport and particle-wall interactions (which are sensitive to the PDMS conditioning) controls the mechanisms of particle capture. Progress in understanding the clogging mechanism in such model filters is an essential first step in controlling fouling of real porous materials.

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