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A NEW MICROFLUIDIC DEVICE INTEGRATED WITH QUARTZ CRYSTAL MICROBALANCE TO MEASURE COLLOIDAL PARTICLE ADHESION

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ABSTRACT

Polystyrene particles simulating bacteria flow down a micro-channel in the presence of potassium chloride solution. Depending on the ionic concentration or flow rates, portion of the particles are trapped on the glass substrate due to intrinsic surface forces. A novel quartz crystal microbalance (QCM) is built into the microfluidic device to track the real-time particle deposition by shift of the resonance frequency. The new technique is promising to quantify water filtration.

Keywords: QCM; Microfluidics; Particle deposition

1. INTRODUCTION

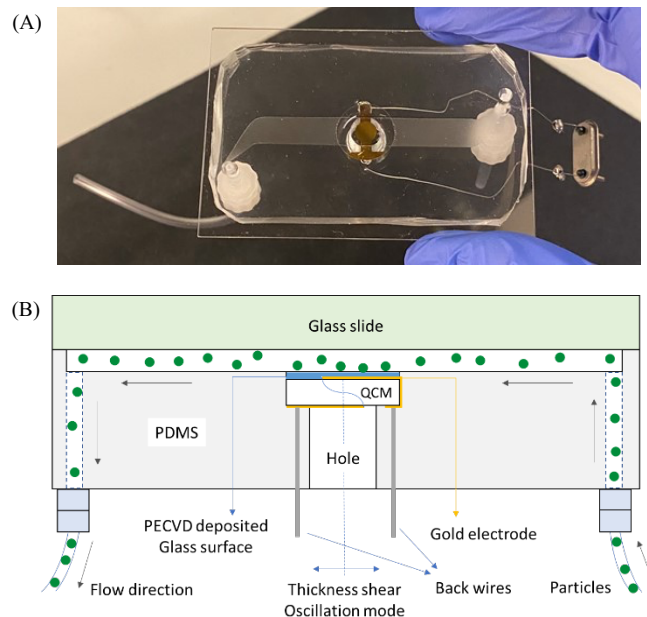
1.1 Colloidal Filtration

Particle adhesion-detachment in a sand column determine the efficacy of filtration. Extensive efforts are made in the scientific community to understand the underlying principle of filtration. The classical colloidal filtration theory describing particle transport in filtration process based on convective-diffusion competition was established in early 70s and met many successes [1]. Intrinsic intersurface forces based on van der Waals and electrostatic double layers are incorporated into the model recently [2,3]. We further investigated the macroscopic transportation and its dependence on the bacterial cell geometry and interaction with sand or glass substrates, the ionic strength of the electrolyte, and the hydrodynamic shear due to flow [4-5].

1.2 Quartz Crystal Microbalance

Quartz crystal microbalance (QCM), resonating in thickness shear mode, is a common sensor to characterize the mass of materials adhered to its surface. The low cost, user friendly, and high-resolution device attracts much attention from the chemical and biological communities [6]. QCM is capable of detecting a mass variation on its surface of less than 10 ng/cm² [7-11]. A

traditional 10 MHz QCM is constructed on an AT-cut quartz crystal plate of 167 μm in thickness. Both sides of the plate are coated with 10 nm chromium to allow further deposition of a 100 nm gold film as the electrodes [12, 13]. Depending on the materials to be investigated, further surface chemical treatment and texture modification are implemented. An applied AC voltage generates a surface resonating transverse shear wave that depends on the QCM crystal orientation and piezoelectric properties. In the presence of an environment, the resonance frequency shifts, $|\Delta f|$, as a result of the addition mass of foreign materials physisorbed or chemisorbed on the sensor surface as well as the viscosity and density of the aqueous medium [14]. Real-time colloidal deposition can thus be characterized.



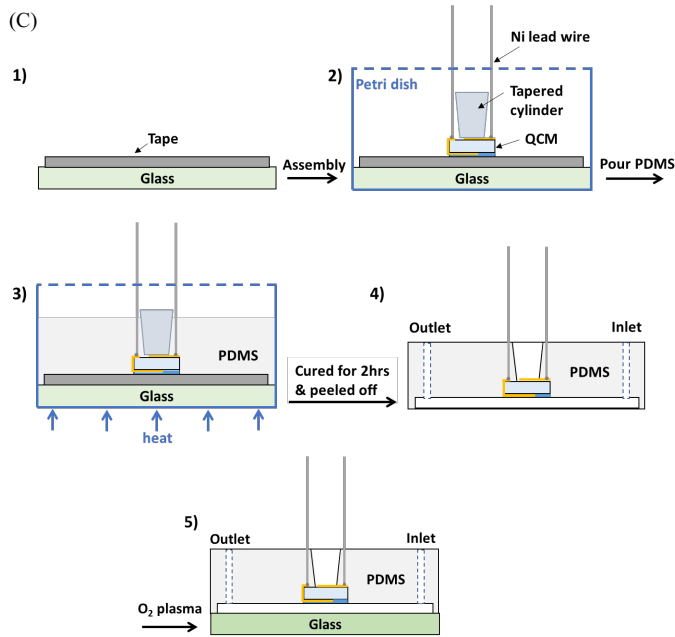


FIGURE 1: (A) QCM-EMBEDDED MICROFLUIDIC DEVICE WITH THE LEAD WIRES FOR FREQUENCY MEASUREMENT AND INLET AND OUTLET FOR PARTICLE-LADEN FLOWS; (B) SCHEMATIC OF THE PARTICLE ADHESION AND DETACHMENT MEASURING MECHANISM BY QCM. (C) SCHEMATIC OF FABRICATION PROCESS.

2. MATERIALS AND METHODS

2.1 Embedded QCM in microfluidic channel

In this research, QCM sensor is integrated into a microfluidic device to study the particle adhesion-detachment on the sand or glass surface of a filtration system. For this purpose, an AT-cut QCM sensor (10 MHz, Fortiming Corp., MA) is coated with a SiO₂ layer (thickness: 413 ± 32 nm) using PECVD method. The fabrication process of the device (shown in Fig. 1(C)) includes the following steps: 1) a scotch tape (3M) of 100 μ m in thickness is mounted onto a glass slide and cut into the desired microchannel shape; 2) the QCM substrate with two soldered Ni lead wires (for connecting with frequency measurement system) is pressed on the tape/glass pair tightly with a 3D printed plastic tapered cylinder and the assembly of QCM/tape/glass is put in a glass petri dish; 3) the mixture of Polydimethylsiloxane (PDMS) precursor and curing agent (Sylgard 184, Dow Corning) with a mixing ratio of 1.2 : 10 is carefully poured into the dish and cured at 100 °C for 2 hrs; 4) after removing the assembly from the dish and peeling off PDMS from the glass slide, two holes are punched with a mechanical puncher (33-32-P/25, Integra, PA) on the PDMS layer to serve as the inlet and outlet of the microchannel; 5) the PDMS/QCM assembly and a glass slide are placed in a O₂ plasma etcher and treated for 1 min and pressed together to form a permanent bond. The microchannel has a rectangular cross-section of 100 μ m \times 6.5 mm. Fig. 1 (A-B) shows a typical device with embedded

QCM sensor with the quick turn tube connectors and its schematic drawing (McMaster-Carr, NJ).

2.2 Experimental set-up and methods

The microfluidic device is fixed on a 3D printed plastics fixture for connecting the flow-in and flow-out tubes. An optical microscope (SM-8, AmScope, CA) held by a mechanical articulator is installed for in-situ observation. The signal is sent to a laptop computer for video recording. The measurement system consists of (Fig. 2) an oscillator (35366-10, ICM, OK), a frequency counter, and a laptop with in-house DAQ (Labview 2011) for data recording. In the experiment, potassium chloride solution KCl (aq) of desirable concentration ranging from $c = 3$ to 30 mM is drawn into the channel by a syringe pump with different flow rates (KdScientific, MA) at the outlet. Plain polystyrene spheres (79633, Sigma-Aldrich., MO) with a diameter of $\sim 5 \pm 1$ μ m and density of 1.05 g/cm³ are introduced into the electrolyte yielding a particle-laden suspension with a particle number density of ~ 900 μ L⁻¹. The suspension is then allowed to flow in the channel and deposited/attached onto QCM surface to study ionic concentrations effect or flowrate effect. Particle deposition on the QCM surface is tracked by the optical microscope and recorded. Transient shift of resonance frequency is monitored throughout the process as a steady state of liquid flow is established.

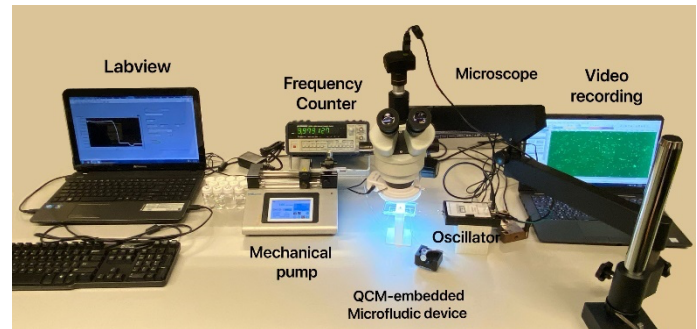


FIGURE 2: EXPERIMENTAL SET-UP FOR PARTICLE ADHESION AND DETACHMENT MEASUREMENT USING QCM SENSOR IN A MICROFLUIDIC DEVICE.

The particle adhesion-detachment is studied under two flow conditions: 1) stagnant flow and 2) intermittent flow. In the stagnant flow, potassium chloride solution KCl (aq) ranging from $c = 3$ to 30 mM is drawn into the channel and halts in stagnant temporarily. Particle-laden suspension prepared in specific KCl (aq) concentration then flows in the channel at a volume flow rate of $Q = 100$ μ L/min for 5 min. The particles are allowed to settle in the stagnant liquid for roughly 10 min. Some particles adhere to the glass substrate (or “collector” in the literature) via natural intersurface attraction. The experiment is ended after the electrolyte flow through the channel for 8 min to remove any particles which were loosely adhered to the QCM surface and PDMS channel surface, as well as the particles left

in the solution close to the inlet tubes. To establish a baseline, a control experiment using deionized (DI) water is performed.

In the intermittent flow study, Potassium chloride solution KCl (aq) of $c = 3$ mM is drawn into the channel and halts in stagnant temporarily. Then flow KCL and particle-laden suspension at 100 $\mu\text{L}/\text{min}$ for 5 min, respectively. After that, the flow rate of particle-laden suspension is reduced to 50 $\mu\text{L}/\text{min}$ and flow lasts for 10 min, then the flow rate is reduced to 10 $\mu\text{L}/\text{min}$ and the flow lasts for 10 min.

2.3 Particles counting

A MATLAB image processing routine (version R2020a, MathWorks, MA) is implemented to count the particles trapped on the QCM post-mortem. Optical micrographs are converted into binary images by applying a critical threshold value of grayscale to outline the silhouette of particle and to distinguish them from the surrounding. Based on the average number of pixels occupied by a single particle, multi-particles aggregates can be differentiated and properly counted. Number of particles hereafter refers to the total number regardless they are isolated or aggregated.

3. RESULTS AND DISCUSSION

3.1 Particle adhesion-detachment for different ionic concentrations in stagnant flow

Fig. 3 shows that the number of adhered particles on the thin SiO_2 surface being a monotonic increasing function of ionic concentration of KCl (aq). In case of DI water in Fig. 4 (A), most particles are washed off without being trapped. An example of number counting by MATLAB is shown in Fig. 4 (F). The number density ρ at fixed c is given in figure caption.

Fig. 4 shows resonance frequency shift as a function of time after onset of flow for a range of KCl (aq) concentration from $c = 0$ (DI water) to 30 mM. Path A-A' and B-B' show the onset and conclusion of liquid flow in the micro-channel. The sudden drop at point B in f originates from the hydrostatic pressure drop due to pumping and goes back at B' after pumping stops.

All the curves follow the similar pattern. At the beginning of the experiment, the particles solutions are drawn into the microchannel at point A by pumping. When the pumping stops at A', the particles are allowed to diffuse to the surface of the QCM and we can observe a sharp decrease of the frequency shift (except for DI water) which is believed to be caused by the adhesion of particles. When the pumping is started again and some of the loosely adhered particles are removed from the surface while the particles left in the solutions near the inlet are introduced to the surface for adhesion. We can see a further decrease of the frequency caused by more particle adhesion (except for 3mM KCl) during this step.

In the presence of DI water, a 1 Hz frequency shift is observed indicating negligible particle adhesion. Particles remain in suspension and keep a distance from the glass substrate and QCM. Bonding with the substrate, if any, is minimal. DI water then flows for another 8 min to remove all particles left in the system. In a steady state, only a small shift of $\Delta f = 4$ Hz is

noted, yet no noticeable particle deposition. The microchannel after each flow test is cleaned with isopropanol followed by DI water, and dried by blowing nitrogen gas. The device is then put in a dry environment for overnight before it is ready for the next test. Increasing ionic concentration shields the electrostatic interaction between negative charged particles and the substrates and thus raises the intersurface attraction. As c increases, more particles are trapped as shown by the frequency shifts $\Delta f = 4$ Hz, 61 Hz, 105 Hz, 144 Hz, to 155 Hz at c indicated in Fig. 4.

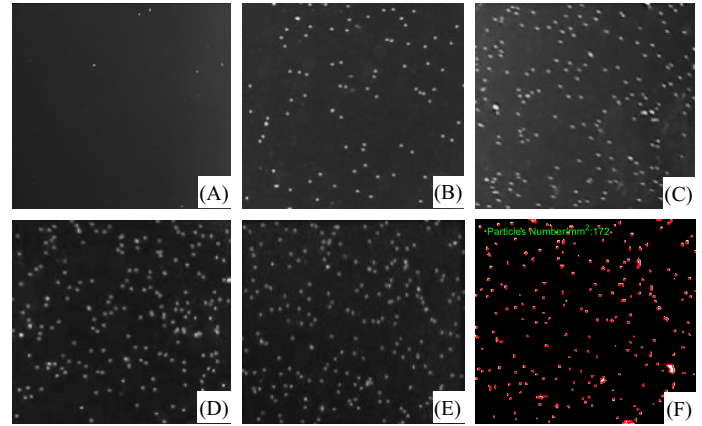


FIGURE 3: PARTICLES ADHERED ONTO QCM SURFACE IN ELECTROLYTES WITH A RANGE OF IONIC CONCENTRATIONS. (A) DI WATER WITH NUMBER DENSITY OF 4 MM^{-2} ; (B) 3MM KCL WITH DENSITY OF 54 MM^{-2} ; (C) 10MM KCL WITH DENSITY OF 126 MM^{-2} ; (D) 20MM KCL WITH DENSITY OF 160 MM^{-2} ; (E) 30MM KCL WITH DENSITY OF 170 MM^{-2} ; (F) AN EXAMPLE OF PARTICLE COUNTING BY MATLAB ROUTINE SHOWING THE SILHOUETTE OF ISOLATED AND AGGREGATED PARTICLES.

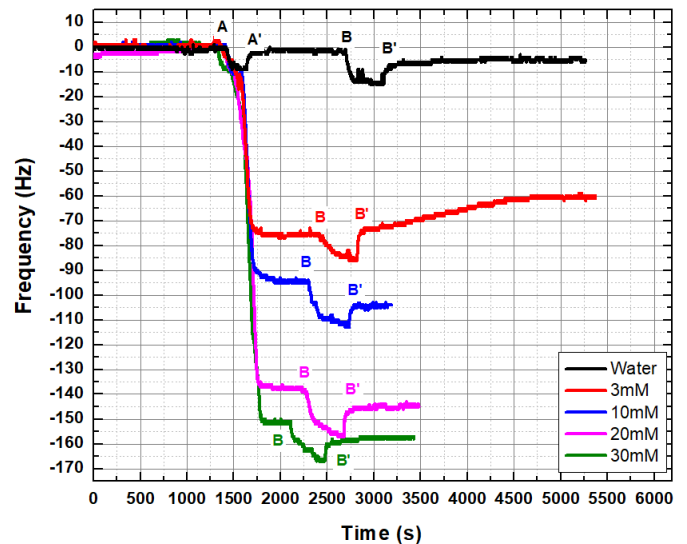


FIGURE 4: REAL-TIME RESONANCE FREQUENCY. PATH A-A' (DI WATER AND ELECTROLYTES ARE MARKED WITH THE SAME COLOR OF A-A'): AT A, ONSET OF PARTICLE-RICH DI WATER/ELECTROLYTES FLOW INTO THE MICROFLUIDIC

CHANNEL; AT A': PUMPING STOPS AFTER 5 MIN; PATH B-B': AT B, ONSET OF ELECTROLYTE WITH SPECIFIC CONCENTRATION FLOWS DOWN THE CHANNEL TO REMOVE ANY TRACE OF PARTICLES LEFT IN THE SYSTEM; AT B', PUMPING HALTS AFTER 8 MIN.

The "Sauerbrey" equation [15] is used to estimate the mass of the adhered particles (Δm) based on the corresponding frequency shift (Δf) and is given by

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (1)$$

where f_0 is the fundamental resonant frequency in Hz, Δf is the frequency shift in Hz, Δm is the additional mass (g), A is the piezoelectrically active crystal area, or area between electrodes in cm^2 , ρ_q is the quartz density ($\rho_q = 2.648 \text{ g/cm}^3$), and μ_q is the shear modulus of quartz for AT-cut crystal ($\mu_q = 2.947 \times 10^{11} \text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-2}$).

The results are presented in Fig. 5, showing frequency shift as a function of KCl concentration, $\Delta f(c)$. Also shown is the number of trapped particle density associated with ionic concentration, $\rho(c)$. QCM measurement is consistent with the optical micrograph of trapped particle distribution. QCM embedded in microfluidic device measures the mass of particles being firmly trapped on the sensor surface (c.f. Fig. 3). Once the particles are trapped, they oscillate synchronously with the surface wave, and the increased inertia due to mass moving through liquid lowers the resonance frequency.

In case of particles with intermediate or large size, a "equivalent mass" (M_p) should be used in equation (1) to replace actual mass ($M > M_p$) of particles [16]. The previous research showed that when the particle with diameter exceeding $30 \mu\text{m}$, the equivalent particle mass $M_p = 2/5 M$ should be used in the equation for estimating the number of particles. While the particle sizes are in nanometer range, we can directly apply Sauerbrey equation with actual mass M [16]. However, the PS particles we are using has a diameter of $5 \mu\text{m}$, there exists no theory for the equivalent mass of the attached particles. We should take an effective mass between M and $2/5 M$ as indicated as dashed/dotted curves in Fig. 5 (A). Particle density fitting shows $\log \rho = 1.71 + 0.32 \log c$ in Fig. 5 (B).

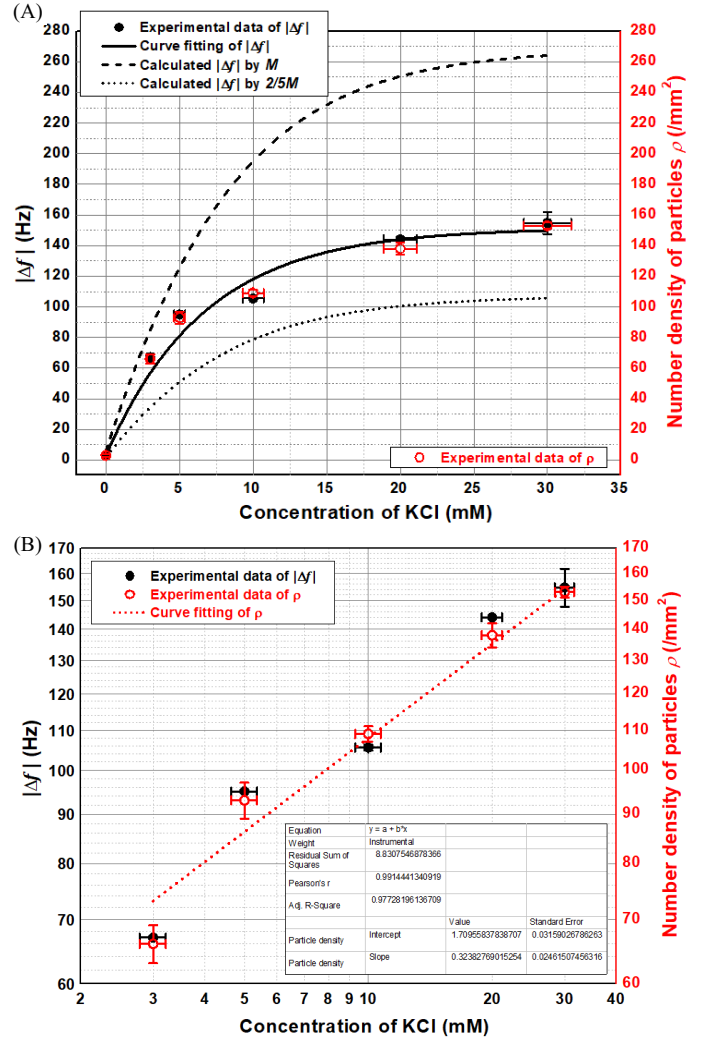


FIGURE 5: (A) FREQUENCY SHIFT AND NUMBER DENSITY OF ADHERED PARTICLES AS A FUNCTION OF KCL CONCENTRATION (THE DASHED/DOTTED CURVES ABOVE AND BELOW THE DATA INDICATED BY THE RANGE FROM SAUERBREY EQUATION. THE UPPER BOUND CORRESPONDS TO THE FULL PARTICLE MASS, WHILE THE LOWER BOUND BEING $2/5$ OF PARTICLE MASS). (B) PARTICLE DENSITY FITTING.

3.2 Particle adhesion-detachment in intermittent flow

Fig. 6 (A) shows the frequency response of the device when the particle solutions prepared in the KCl concentrations of 10 mM and 20 mM flow in the microchannel at flow rates of 100 $\mu\text{l/min}$, 75 $\mu\text{l/min}$, 50 $\mu\text{l/min}$, 20 $\mu\text{l/min}$ and 10 $\mu\text{l/min}$. The relationship between the rate of change in frequency ($|K|$) which is related to the rate of particles adhering and the flow rate which is the indication of shear force acting on the particles is shown in Fig. 6 (B). As can be seen, the particles adhered at a higher rate when flow rate is lower (u) and the data fitting shows correlation $\log |K| = 0.9949 - 0.8216 \log u$ for 3mM KCl, and $\log |K| = 1.1646 - 0.8769 \log u$ for 10mM KCl in Fig. 6 (B). More quantitative analysis is under development. The adhesion of

particles on the SiO₂ surface for the flow rates of 100 $\mu\text{l}/\text{min}$, 50 $\mu\text{l}/\text{min}$ and 10 $\mu\text{l}/\text{min}$ are displayed in Fig. 6 (C).

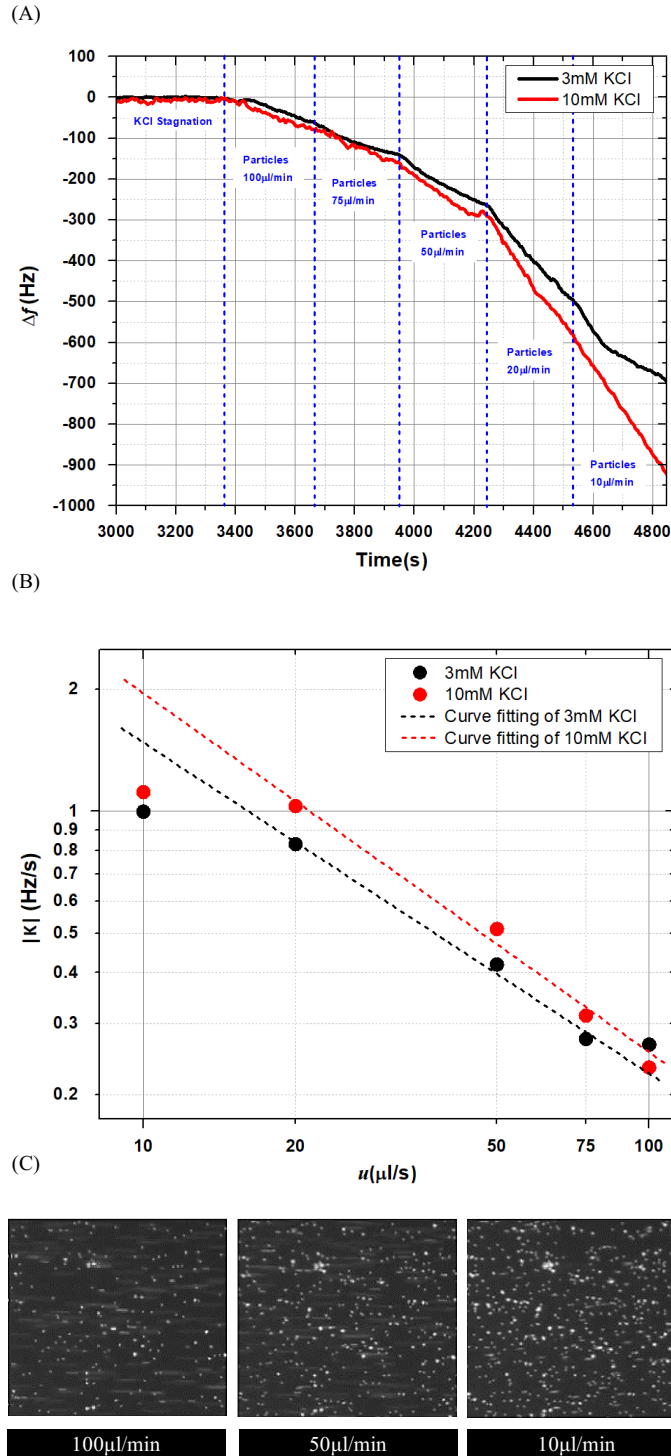


FIGURE 6: (A) FREQUENCY SHIFT OF QCM VS. TIME FOR PARTICLE SOLUTIONS FLOWING AT DIFFERENT FLOW RATES AND KCL CONCENTIONS (B) RATE OF CHANGE IN QCM FREQUENCY SHIFT VS. FLOW RATE (C) PHOTOS OF

ADHERED PARTICLES ON SiO₂ SURFACE AT DIFFERENT FLOW RATES

4. CONCLUSION

Microfluidic device with an embedded QCM is a new technique to characterize real-time colloidal particle deposition in the presence of an electrolyte. The higher the ionic concentration, the more particles are trapped due to intrinsic intersurface attraction at the channel wall. Besides, particles are trapped faster in lower flow rate, which is consistent with our expectation.

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