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A polymer based sensor for phosphate detection in water

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***Abstract*— This paper presents the detection of phosphate (PO_4^{-3}) concentration in water by using a commercial quartz crystal microbalance (QCM) sensor that was coated with a novel polymeric affinity layer for the first time. The QCM sensor was exposed to PO_4^{-3} and chloride (Cl^-) solutions in various concentrations to investigate the sensitivity of the affinity layer. Changes in the viscosity of a solution, and weak binding of ions onto the polymeric layer eliminated the effect of PO_4^{-3} binding to the polymer and hardened the concentration detection. Therefore, we have proposed a new method in which an intermediate Cl^- solution is applied before introducing the PO_4^{-3} solution to detect the concentration level in a continuous flow.**

Keywords—Quartz crystal microbalance sensor; polymeric affinity layer, phosphate detection, viscosity, mass binding

I. INTRODUCTION

Phosphorus is an essential nutrient for plants and animals that is available in rock and soil minerals, as well as fertilizers, sewage and detergents [1]. The release of phosphorus in rivers' water and lakes due to weathering or waste pollution will results in the over enrichment of phosphate ions (PO_4^{-3}). This increase can cause massive growth of plankton and aquatic plants which leads to an eutrophication process [2].

Wastewater discharge from sewage treatment plants contributes the largest proportion of the phosphorus in rivers [3]. For this reason, the presence of PO_4^{-3} in river water with concentrations greater than 0.1 mg/L is not permitted by the European Water Framework Directive, and needs to be carefully monitored [4]. The currently available instruments for collecting water quality data from fields such as automatic samplers, portable and fixed site water quality monitors are cumbersome and not accurate [5].

Cantilever-based and quartz crystal microbalance (QCM) sensors are the two mass-sensing options [6] for phosphate detection, however, the damping of the output signal of cantilever-based sensors in liquid made them unsuitable for commercial use even with their high sensitivity [6, 7]. QCM sensors are the best option for phosphate detection in water, and they are capable of rapid, sensitive, and cost effective detection of various types of biological and chemical molecules in liquid [8, 9]. A QCM sensor consists of a thin disk of quartz with parallel circular electrodes patterned on both sides. The front side is in contact with the analyte of interest and the backside is exposed to air [10]. The QCM sensor operates by applying a potential across the electrodes and generating a shear force. The quartz crystal resonates as electromechanical standing waves are created [10]. The QCM sensor measures a mass per unit area by measuring the change in resonance frequency, f_0. The mass responsivity of the QCM sensor is calculated as following based on the Sauerbrey equation [11]:

$$\frac{\Delta m}{\Delta f} = -\frac{A_{piezo}(\mu_q \rho_q)^{0.5}}{2f_0^2} \tag{1}$$

where Δm is the adsorbed mass, Δf is changes in frequency, A_{piezo} is the active sensing area, and μ_q and ρ_q are shear modulus and density of quartz, respectively.

The above equation is correct for the added solid layers onto the QCM sensor, but in the case of adding a soft layer such as polymer and performing a measurement in liquid, the changes in the energy dissipation of the oscillating system will violate the linear relation between Δf and Δm. In this case, the following equation should be considered to include the liquid viscosity, η_l, and liquid density, ρ_l [11]:

$$\Delta f = -f_0^{1.5}\sqrt{\frac{\eta_l \rho_l}{\pi \mu_q \rho_q}} \tag{2}$$

The schematic of the QCM sensor and the added polymeric affinity layer is shown in Fig. 1.

II. METHODOLOGY

We aim to provide detection of PO_4^{-3} concentration in water by using a polymeric affinity layer spin coated onto a QCM sensor. The commercial gold coated 5 MHz crystals (Q-Sense sensors, Biolin Scientific) [12] have been used in our experiments.

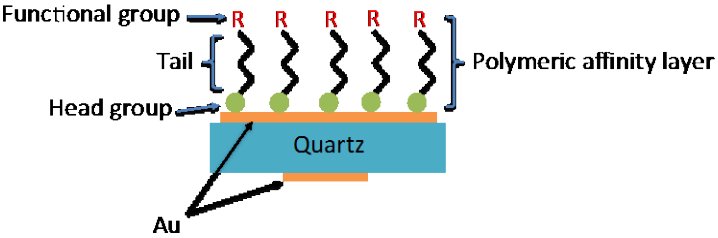

Fig. 1. The schematic of the added polymeric affinity layer on top of a QCM sensor.

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At the start of the experiment, the polymer coated QCM sensor is exposed to ultra high quality (UHQ) water to measure the baseline. This is followed by an injection of a PO_4^{-3} solution, and this process is repeated for a number of cycles. Other solutions including diluted hydrochloric acid (HCl, 0.1M), Sodium Chloride (NaCl, 0.1M), and Calcium Chloride ($CaCl_2$, 0.05M)) have also been applied to investigate the polymer response to changes in solution ionic strength.

The polymeric layer has been spin coated onto the QCM sensors at 3000 rpm for 20 sec. Prior to the coating step, the crystals were cleaned by sonication using acetone and isopropyl alcohol followed by rinsing in ultra high quality (UHQ) water, and nitrogen drying.

III. RESULTS AND DISCUSSION

The measurement setup (Fig. 2) consists of a flow cell constantly fed using solutions of PO_4^{-3} or HCl in water at different concentrations with the help of a peristaltic pump. Two flow rates of 1.9 and 3.9 mL/min have been used during the experiments. A QCM instrument (eQCM 10M, Gamry Instruments) [13] was used for reading the frequency changes versus time.

A. *Phosphate-water cyclic experiment*

Fig. 3 shows the change in frequency of the sensor in response to the cyclic feeding of UHQ followed by a PO_4^{-3} solution at concentrations of 0.001 and 0.1 mg/L over time. The grey areas in the figures represent the period that the pump was left ON with the flow rate of 1.9 mL/min. Changes in the room temperature and hydration of the polymer layer in solution causes a decreasing slope throughout the experiment for both phosphate concentrations. By the introduction of phosphate solution, the Cl^- functional groups will be replaced by PO_4^{-3} with larger molar mass via an ion exchange process. The introduction of a 0.001 mg/L PO_4^{-3} solution after a UHQ water cycle results in negative changes in the resonance frequency due to the binding of PO_4^{-3} to the polymer surface. No slope changes were observed when the cycle was performed using a 0.1 mg/L PO_4^{-3} solution.

B. *Introducing a new method for phosphate detection in a continous flow*

To confirm the effect of the PO_4^{-3} molecules interaction on the frequency increase solely, we introduced different chloride solutions (i.e. HCl, NaCl, and $CaCl_2$) keeping the molarity of Cl^- ions constant. No slope changes were expected by applying Cl^- solutions as the polymer surface is terminated by chloride ions.

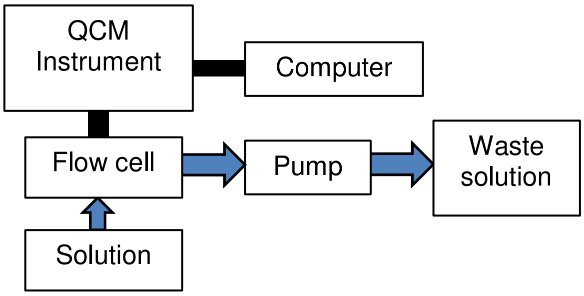
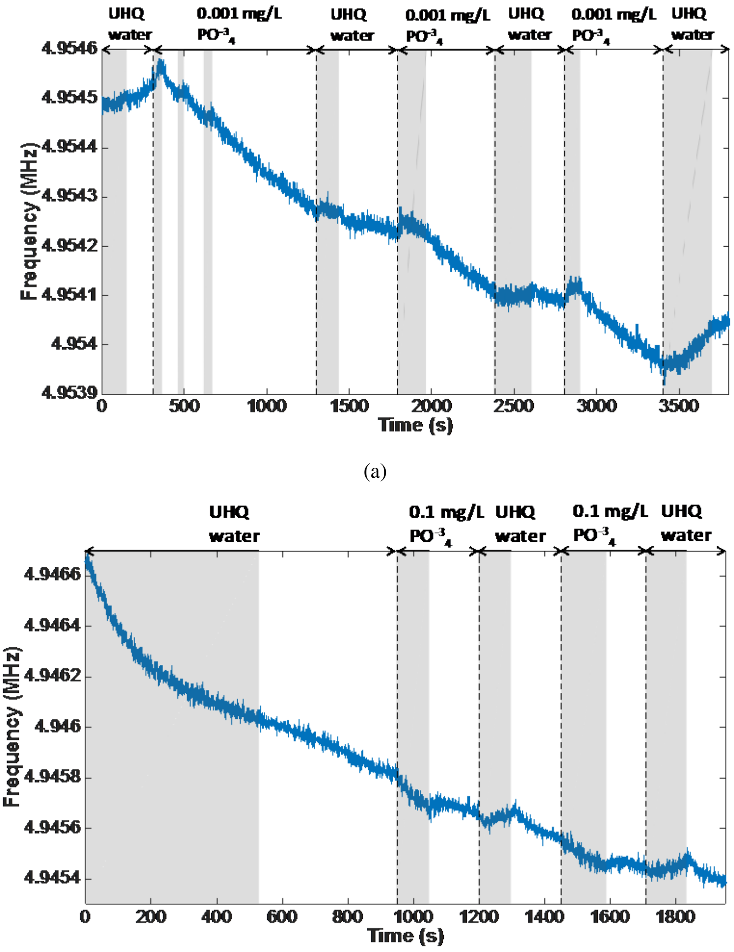


Fig. 2. The measurement setup.



(a)

(b)

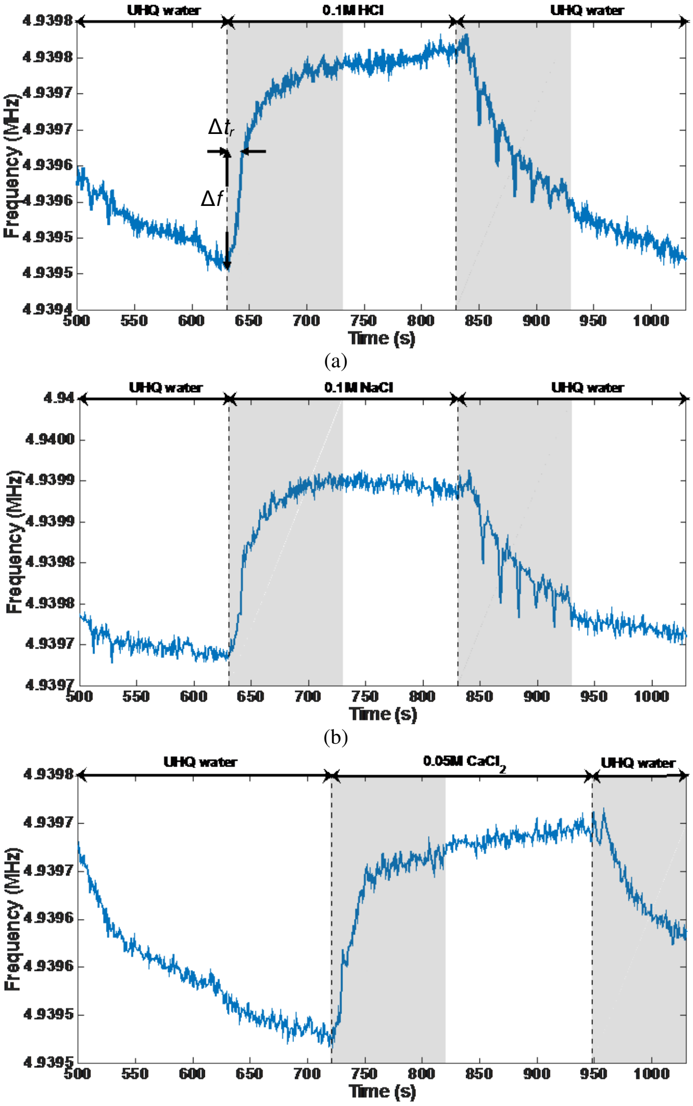
Fig. 3. Cyclic UHQ-PO_4^{-3} solution experiment of the polymer coated QCM sensor for: (a) 0.001 mg/L, and (b) 0.1 mg/L phosphate concentrations.

Fig. 4 shows the response of the coated QCM sensor to Cl^- solutions in cyclic UHQ-Cl^- solution experiments. The pump was left ON with the flow rate of 1.9 mL/min during the grey intervals in Fig. 4. The positive resonance frequency change of ≈150 Hz has been seen for all the Cl^- solutions. This change is owing to molecular interactions in the solid-liquid interface of the sensor that result in reduction of the viscosity of the liquid due to shear thinning in the interface [14], and weak binding of positive ions to the surface of the sensor [15, 16]. Table I presents the frequency change over time ($\Delta f/\Delta t_r$) for all Cl^- solutions in Fig. 4. As $\Delta f/\Delta t_r$ shows the maximum slope after adding Cl^- solution, Δt_r presents the time interval between the time of applying Cl^- solution and the time that the slope starts to reduce. Similarly, Δf is the frequency changes between these two points. Table I shows similar level of sensitivity for all Cl^- solutions.

A cyclic experiment performed using an uncoated QCM sensor exposed to HCl solution (Fig. 5), it showed that the positive frequency change observed in the presence of the polymer is reduced to ≈40 Hz with no polymer. This is because of the viscosity changes at the interface, as no binding should happen on the sensor surface when there is no polymer coating.

A similar frequency change for the HCl solution in Fig. 5 happened for the 0.1 mg/L PO_4^{-3} solution in Fig. 3. This frequency change in different direction has cancelled out the effect of PO_4^{-3} binding to the polymer layer. Therefore, applying intermediate Cl^- solutions to the polymer surface before introducing PO_4^{-3} solution will improve the detection of changes in frequency.

Fig. 6 shows the response of QCM sensor to a full cyclic experiment using UHQ-HCl-PO_4^{-3} solution fed in that particular order. The pump was left ON with the flow rate of about 3.9 mL/min during the experiment. Injecting the 0.01 mg/L PO_4^{-3} solution results in the sensitivity of $\Delta f/\Delta t_r$=45. The sensitivity has been calculated as explained for Fig. 4. The required time for the polymer to be saturated by the phosphate ions, Δt_s, has been calculated from Fig. 6 to be about 627 s. The sensor response in Fig. 6 demonstrates that conditioning using HCl solution previous to introducing the PO_4^{-3} solution is essential to detect mass binding to the polymer coated QCM sensor.



(a)

(b)

(c)

Fig. 4. The response of polymer coated QCM sensor to various chloride solutions: (a) 0.1M HCl, (b) 0.1M NaCl, and (c) 0.05M $CaCl_2$

TABLE I. THE SENSITIVITY OF THE POLYMER LAYER TO VARIOUS CHLORIDE SOLUTIONS

Solution	$\Delta f/\Delta t_r$
0.1M HCl	13.45
0.1M NaCl	9.81
0.05M $CaCl_2$	10.63

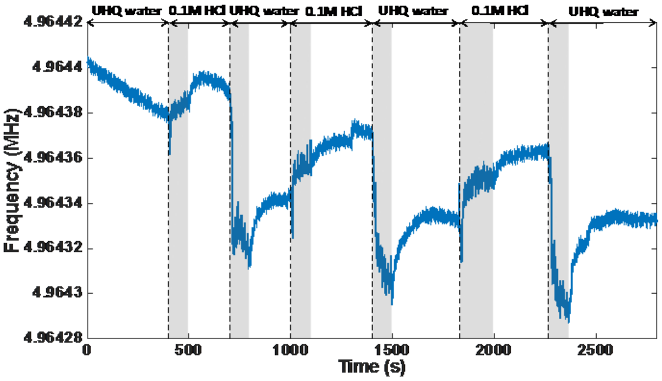
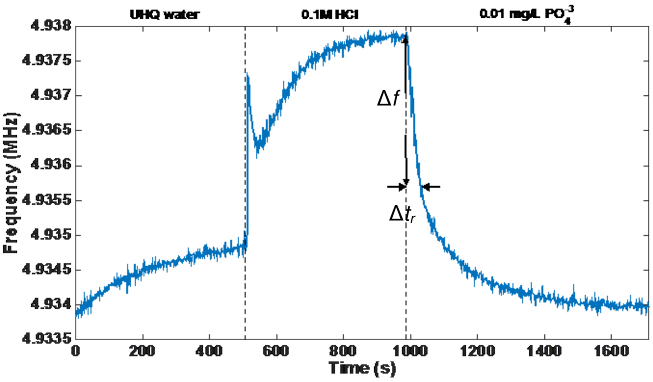


Fig. 5. Cyclic UHQ-HCl experiment of the uncoated QCM sensor.



(a)

Fig. 6. The response of polymer coated QCM sensor to UHQ-HCl-PO_4^{-3} solution experiment for 0.01 mg/L phosphate concentrations.

CONCLUSION

This paper presents a new cyclic experiment technique to characterize the sensitivity of the QCM sensor to different concentrations of phosphate in water by using a novel polymeric affinity layer spun coated onto the sensor. The introduction of intermediate Cl^- solutions to the polymer surface before introducing PO_4^{-3} solution will ease the detection of changes in frequency in the presence of a continuous flow. This technique will be applied to our future designed QCM-based sensor for sensing various pollutants in river water. Increasing the sensitivity of the polymer layer to the pollutants while keeping the saturation time as long as possible is considered in our future work.

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