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Preparation of MIP-based QCM nanosensor for detection of caffeic acid

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ABSTRACT

In the present work, a new caffeic acid imprinted quartz crystal microbalance (QCM) nanosensor has been designed for selective assignation of caffeic acid in plant materials. Methacrylamidoantipyrine-iron (III) [MAAP-Fe(III)] as metal-chelating monomer has been used to prepare selective molecular imprinted polymer (MIP). MIP film for detection of caffeic acid has been developed on QCM electrode and selectivity experiments and analytical performance of caffeic acid imprinted QCM nanosensor has been studied. The caffeic acid imprinted QCM nanosensor has been characterized by AFM. After the characterization studies, imprinted and non-imprinted nanosensors was connected to QCM system for studies of connection of the target molecule, selectivity and the detection of amount of target molecule in real samples. The detection limit was found to be 7.8 nM. The value of Langmuir constant (b) (4.06×10^6) that was acquired using Langmuir graph demonstrated that the affinity of binding sites was strong. Also, selectivity of prepared caffeic acid imprinted nanosensor was found as being high compared to chlorogenic acid. Finally, the caffeic acid levels in plant materials was determined by the prepared QCM nanosensor.

1. Introduction

Phenolic compounds are secondary plant metabolites and naturally present in almost all plant materials, including food products of plant origin. These compounds are thought to be an integral part of both human and animal diets [1]. In addition, they display many biological properties such as anti-inflammatory, antiallergic, antibacterial, antimicrobial, cardioprotective, and antioxidant activities [2]. Moreover, they have been associated with health benefits provided by the consumption of fruits and vegetables [3].

Caffeic acid (3,4-dihydroxycinnamic acid) is one of the natural phenolic compounds widely scattered in plant-derived materials such as fruits, vegetables, tea, coffee, wine, olive oil etc. [4,5]. Caffeic acid (CA) is known to exhibit a wide variety of biological functions, including antioxidant, anti-inflammatory, antimetastatic, antimutagenic, antidepressive, antianxiety, anticarcinogenic activities and inhibition of HIV replication [5–8].

Several analytical methods including liquid chromatography–mass spectrometer (LC–MS) [9], gas chromatography–mass spectrometer (GC–MS) [10], thin-layer chromatography (TLC) [11] and capillary electrophoresis (CE) [12] have been employed for the determination of phenolic acids in food samples and plant materials. In the literature, various methods are used for analysing of caffeic acid such as a capillary gas chromatographic method [13], voltammetric method [14], liquid chromatography–electrospray ionization mass spectrometry [15], capillary electrophoresis [16], high pressure liquid chromatography (HPLC) [17,18]. It can be said that these methods are relatively expensive and require pretreatment.

The quartz crystal microbalance (QCM) is a simple, cost-effective, high-resolution mass sensing technique [19] which has been favorably adopted for analytical application due to its extreme sensitivity to the nanogram level of mass change loaded onto the surface of the QCM resonator [20]. The increased mass, associated with the binding reaction, results in a decrease of the oscillating frequency [21]. QCM has been widely used in biochemistry, environment, food, and clinical analyse because the instrument provides a label-less method for the direct study of biospecific interaction process [22–26]. With immobilized antibodies on the surface of crystal, some QCM immunosensors have been employed for the detection of viruses [27], bacteria [28], and DNA [29]. However, there is no specific selectivity [30]. As a result, various chemicals and biomaterials have been used to modify (physically or chemically) the QCM surface in an effort to obtain selectivity [31].

Molecular imprinting is a technique which can be used to obtain selective layer on the QCM electrode surface. Molecular imprinting is a promising technique for the preparation of polymers which possess specific recognition sites. By means of a

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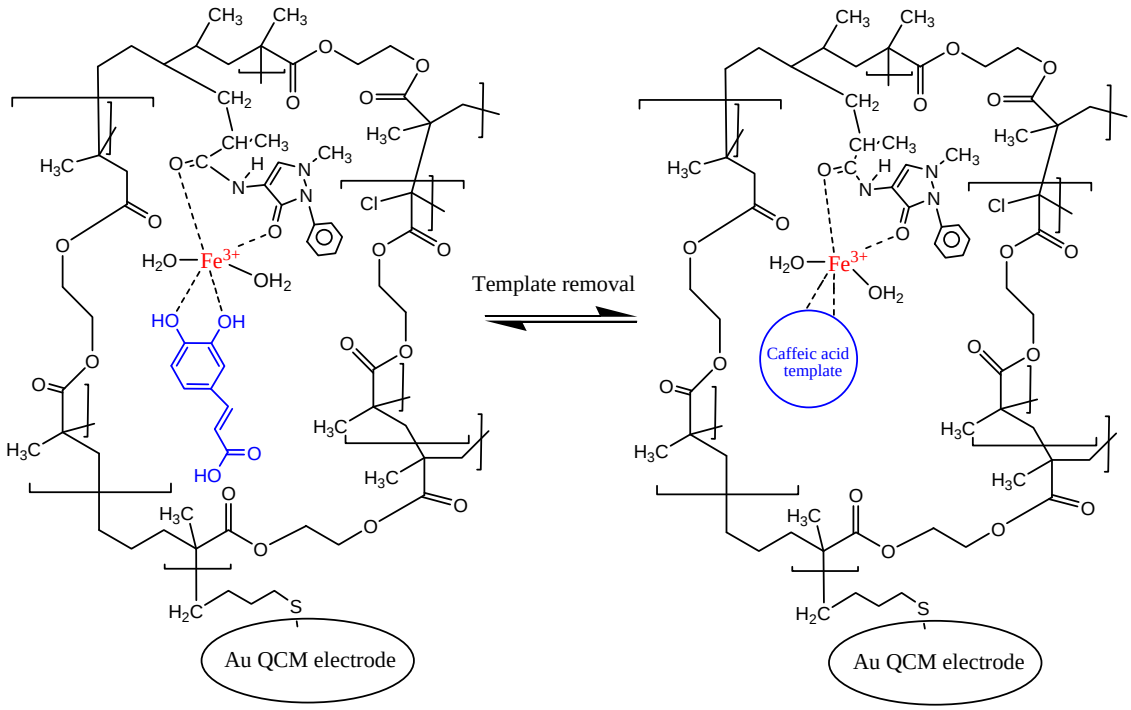

Fig. 1. Schematic illustration of caffeic acid molecular imprinting on allyl mercaptan modified Au QCM electrode.

synthetic organic polymer matrix, the imprints of the template molecule are created in the polymer. After the template is eluted from the rigid polymer network, recognition sites complementary to the template molecule in shape and size can be obtained [20]. The molecularly imprinted polymers (MIPs) represent robust and stable artificial receptors for analyte of interest. The fabrication of a MIP film to detect certain compounds via a QCM transducer has been accomplished in recent years due to its attractive performance, such as high selectivity, real-time and on-line capabilities. Because of these favorable properties of the technique, the combination of QCM and molecular imprinting polymers (MIPs) have been used to the determination of different molecules such as albumin which is a major blood plasma protein [32], 8OHdG which has been identified as a biomarker in oxidative stress [30], and nucleobases for DNA/RNA detection [21], Cu(II) ions in solution [20], folic acid [33] and nerve agent such as paraoxon [34].

Although the fabrication of MIPs to detect certain compound via QCM has been accomplished in recent years, to the best of our knowledge, there is not any report for detection of caffeic acid based MIP-QCM system. In this study, we describe a new, sensitive, method for the generation of MIP on QCM crystal to determine caffeic acid. The method is based on polymerization of a metal-chelating monomer in the presence of the template molecule (caffeic acid), which can produce molecularly imprinted polymer coating on QCM crystal. The prepared QCM nanosensor is used to detect caffeic acid in plant materials to understand the suitability of the prepared nanosensor in real samples.

2. Experimental

2.1. Chemicals

Caffeic acid, azobisisobutyronitrile (AIBN), ethanol (absolute) and allyl mercaptan were supplied from Aldrich Chem. Co. (Milwaukee, WI, USA). EDMA was obtained from Fluka A.G. (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroguanin inhibitor and stored at 4 °C until use. All other chemicals were of reagent grade and purchased from Merck AG (Darmstadt, Germany). All water used in experiments were obtained from Zeneer Power II water purification system.

2.2. Instruments

An AT-cut, gold/Cr polished, 5 MHz quartz crystals and a quartz crystal analyzer (SRS Standford Research Systems, Model QCM200 Quartz Crystal Microbalance Digital Controller) are used to perform microgravimetric measurements. Saurbrey's equation has been established for an AT-cut shear mode QCM

$$\Delta F = \frac{-2 F_o^2 \ \Delta m}{A (p_q \mu_q)^{1/2}} \quad (1)$$

where ΔF is the measured frequency shift due to the added mass in Hertz, F_0 is the fundamental oscillation frequency of the dry crystal, Δm is the surface mass loading in grams, p_q is the density of quartz (2.65 g cm^{-3}), μ_q is the shear modulus (2.95 × 1011 dyn cm^{-2}), and A is the electrode area (0.19 ± 0.01 cm^2). For the 5 MHz quartz crystals used in this work, Eq. (1) estimated that a frequency change of 1 Hz corresponds to a mass increase of 1.03 ng cm^{-2} on the electrode [35].

2.3. Preparation of metal-chelate monomers and caffeic acid (CA) having pre-organized complexes

Methacrylamidoantipyrine (MAAP) monomer which has π electron-rich aromatic ring was synthesized for our last studies using antipyrine which is hydroxy radical capture and spectroscopic reagent for phenols and characterized according to the previously published procedure [36]. Then, we have combined molecular imprinting with the ability of methacryloyl antipyrine (MAAP) to chelate metal ions (Fe(III)) which form good complex with caffeic acid [37,38] to create active centrum on polymer. In the same manner, metal-chelate monomer, methacrylamidoantipyrine-iron(III) [MAAP-Fe(III)], was synthesized and characterized with respect to the published procedure [39]. Ligand exchange

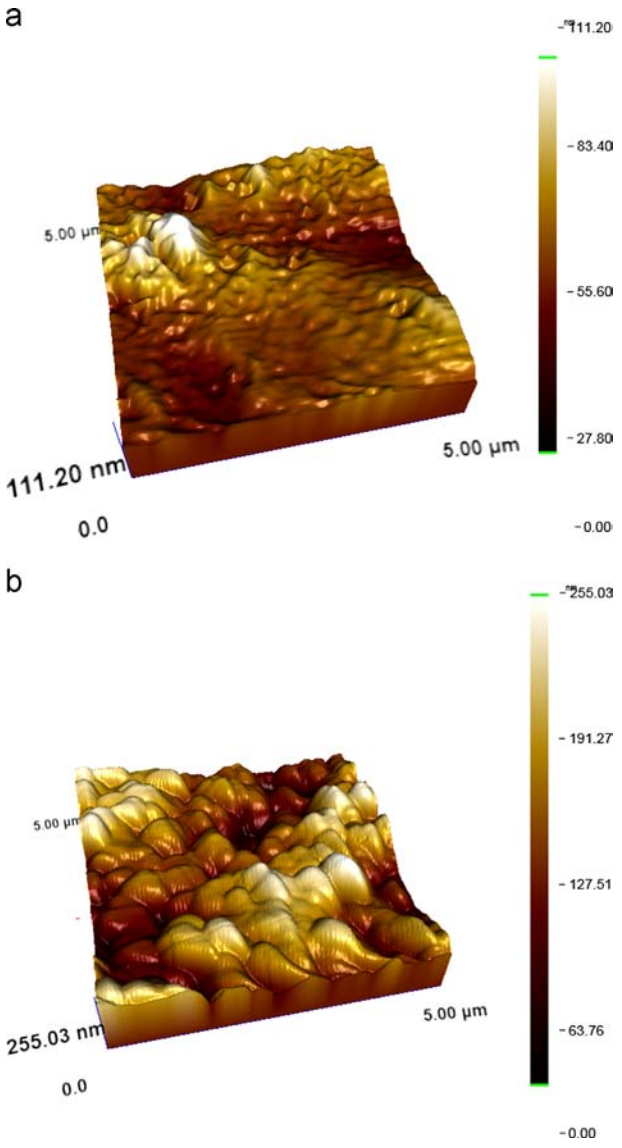

Fig. 2. AFM image of (a) NIP and (b) MIP coated QCM electrode. Scanning mod: Dynamic, Scanning area: 5.0 × 5.0 μm.

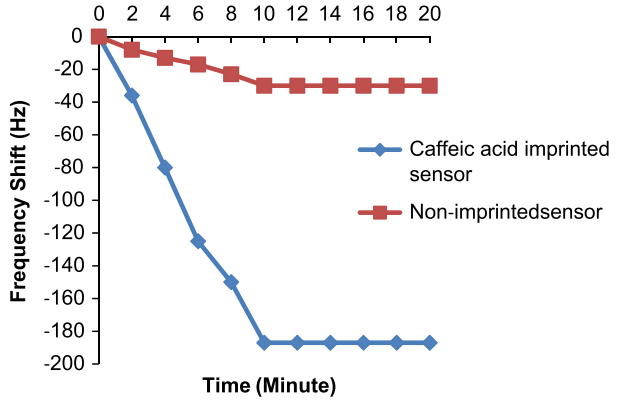

Fig. 3. QCM responses of the caffeic acid imprinted and non-imprinted nanosensors (C_{CA}=0.1 μM).

monomer, methacrylamidoantipyrine-iron(III)/caffeic acid [MAAP-Fe(III)/CA] was synthesized using MAAP-Fe(III) and template caffeic acid. MAAP-Fe(III) (0.01 mmol) and caffeic acid (0.01 mmol) were

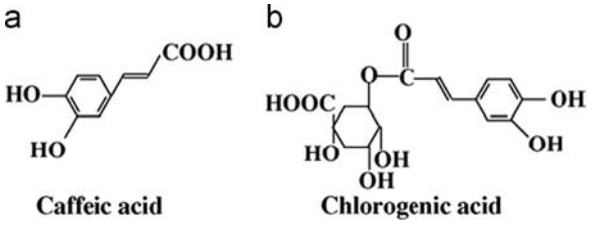

Fig. 4. Chemical structure of (a) caffeic acid and (b) chlorogenic acid.

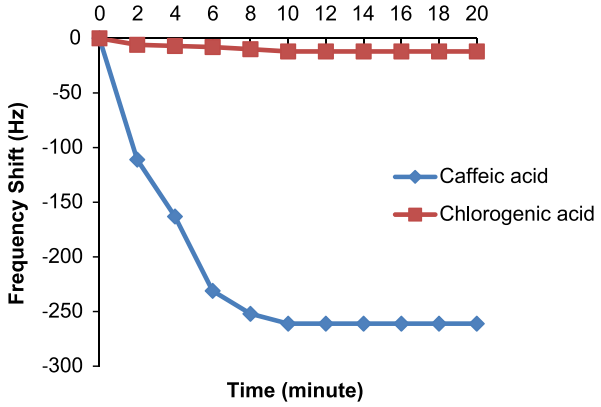

Fig. 5. QCM responses of the caffeic acid imprinted nanosensors for caffeic acid and chlorogenic acid (all concentrations are 100 μM).

Table 1
Selectivity of caffeic acid imprinted QCM nanosensor.

	Q (mg/g) (Imprinted)	Q (mg/g) (Non-imprinted)	*k* (Imprinted)	*k* (Non-imprinted)	*k*′
Caffeic acid	16.03	0.92			
Chlorogenic acid	0.73	0.55	21.77	1.67	13

dissolved in ethanol and the two solutions were added each other, then final solution was stirred 24 h. When caffeic acid has been added into the monomer system, a –OH stretching vibration (2500–3000 cm^{-1}) of –COOH functional group and a broad OH band (3200–3550 cm^{-1}) which became apparent due to –OH group of phenol, in chemical structure of caffeic acid, was observed from the FT-IR spectra. Both infrared frequencies and color change (while solution of MAAP-Fe(III) monomer system is yellow, after adding caffeic acid into the solution, color has changed to green) in solutions demonstrate the interaction between MAAP-Fe(III) and caffeic acid.

2.4. Preparation of the caffeic acid imprinted polymer nanosensor

Before coating, gold surfaces were cleaned in piranha solution (1:3 30% H_2O_2/concentrated H_2SO_4). In order to insert thiol groups onto the gold surface of the QCM electrode, the cleaned surfaces were dipped into allyl mercaptan solution (2-propene-1-thiol) (0.30 mmol) for 24 h. The thiol group of allyl mercaptan directed the interaction between the QCM gold surface and imprinted polymer and the allyl group of allyl mercaptan procures the polymerization of metal-chelate monomer from this site. The electrode was then washed with ethanol and deionized water to remove the excess of thiols.

For the polymerization, the reaction mixture containing the metal-chelate (MAAP-Fe(III)-CA) pre-organized monomer, EDMA crosslinking monomer and initiator (AIBN) in ethanol was prepared. Then, a small amount of reaction mixture was dripped onto the allyactivated QCM electrode. Polymerization was carried out at

Table 2
Quantities of caffeic acid in plant materials (mg caffeic acid/kg material).

Used method	Centaury	Sage	Black tea	Apple	Potato
CA imprinted QCM sensor	70.15	32.46	3.76	0.0012	0.0272
HPLC	61.35	41.50	2.81	0.0650	0.0470

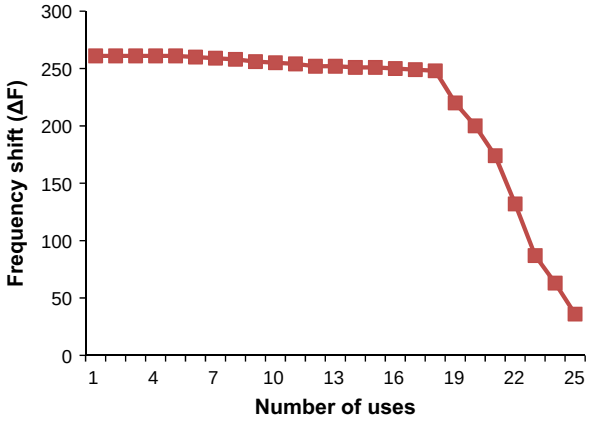

Fig. 6. Functional stability of the caffeic acid imprinted QCM nanosensor.

room temperature under UV light irradiation for 4 h (Fig. 1). As a reference, the nonimprinted polymer-coated QCM sensors (NIP) were also prepared in a similar manner as with MAAP-Fe(III).

Fig. 2 shows AFM images of NIP and MIP coated gold electrodes. The surface roughness values of NIP and MIP coated QCM electrodes were determined as 8.24 and 42.85 nm, respectively. The roughness of the surface is well distributed through all surface of the electrode. This result shows that the homogen caffeic acid imprinting on the QCM electrode has been successfully realised. This feature is one of the significant parameters to control the selectivity and recognition rate of the sensor.

2.5. Monitoring of imprinted QCM nanosensor response

Caffeic acid imprinted QCM nanosensor was used for real time detection of caffeic acid. The caffeic acid was dissolved in ethanol and the frequency of the nanosensor was monitored until it became stable. The frequency shift for each concentration (0.01–1000 μM) of caffeic acid was calculated using the equation $\Delta F = F_0 - F_1$ and the evaluation was performed in triplicate. After each analysis, the desorption process was applied using methanol/glacial acetic acid (9:1, v/v) (Fig. 1) [40]. After desorption step, the caffeic acid imprinted QCM nanosensor was washed with deionized water. This washing process was repeated until the frequency of the nanosensor recovered to the F_0 value.

2.6. Selectivity of MIP coated QCM nanosensor

The selectivity of the prepared nanosensor for caffeic acid was estimated using chlorogenic acid which is similar in chemical structure with caffeic acid. The concentration of competitive molecule obtained 100 μM in ethanol. QCM nanosensor was treated with this competitive molecule. After the equilibrium, the frequency shift of chlorogenic acid measured by designed caffeic acid imprinted QCM nanosensor and Δm and Q (nmol) values were calculated with regard to Eq. (1). The selectivity coefficient for the binding of caffeic acid in the occurrence of opponent species can be acquired from equilibrium binding data consistent $k = Q_{\text{template molecule}}/Q_{\text{opponent species}}$. The relative selectivity coefficient ($k' = k_{\text{imprinted}}/k_{\text{non-imprinted}}$) results from the comparison of the k values of the imprinted polymer with non-imprinted polymers.

3. Results and discussion

3.1. Measurement of binding interaction of molecularly imprinted QCM nanosensor via ligand interaction

The binding of caffeic acid to the caffeic acid imprinted metal-chelate polymer [MAAP-Fe(III)] on a gold quartz crystal induce a mass change, Δm, that was reflected in the crystal frequency. The QCM electrodes were washed with deionized water and then dried. The frequency (F_0) was monitored in an open space indoor environment after drying and then caffeic acid solution was dripped on a confined type detector cell [41]. The frequency of the nanosensor decreased after adding caffeic acid solution, then reached the constant value in 10 min (Fig. 3). It can be seen that the reaction reached equilibrium rapidly suggesting stronger caffeic acid molecules interaction to with the imprinted polymer on the quartz crystal. When non-imprinted polymer was used, less binding of caffeic acid molecules to non-imprinted polymer was observed.

The binding interaction and equilibrium information between imprinted polymer and caffeic acid template can be acquired by Langmuir isotherm. This analysis employs the following equation:

$$\frac{1}{Q} = \left(\frac{1}{[Q_{\max} \times b]} \times \frac{1}{C}\right) + \frac{1}{[Q_{\max}]} \quad (2)$$

where Q is the amount of caffeic acid bound to polymer, as calculated by the mass frequency variation upon addition of analyte, and C is the concentration of free caffeic acid. $Q_{\max}$ represents the apparent maximum number of binding sites, and b is the Langmuir constant. The results obtained from linearized form of the Langmuir isotherm by plotting $1/Q$ as a function of $1/C$ is

$$\frac{1}{Q} = \left(0.0065 \times \frac{1}{C}\right) + 0.0264$$

Hence, Langmuir constant, b, and the apparent maximum number of recognition sites, $Q_{\max}$, values for the specific interaction between the template imprinted polymer and the template itself were 4.06×10^6 and 37.88, respectively. The high value of Langmuir constant (b) suggests that affinity of the binding sites is very strong.

3.2. Selectivity studies of imprinted polymer on QCM nanosensor

The adsorption of chlorogenic acid, which is similar in chemical structure with caffeic acid (Fig. 4), on the imprinted quartz crystal nanosensor was examined for a better understanding of interactions between the binding sites of MIP-QCM nanosensor and its template molecules, and the ability of this imprinted polymer to identify the caffeic acid molecules.

The adsorption capacity of caffeic acid imprinted polymers for adsorption of caffeic acid plus related molecule chlorogenic acid was evaluated (Fig. 5). According to experimental studies; Q values of caffeic acid and chlorogenic acid were determined as 16.03 and 0.73 mg g^{-1} for MIP nanosensor and 0.92 and 0.55 mg g^{-1} for NIP nanosensor, respectively. Selectivity coefficients (k) and relative selectivity coefficients (k') values are displayed in Table 1. As shown in Table 1, MIP nanosensor was 22 times more selective for caffeic acid than for chlorogenic acid.

3.3. Analytical performances

The calibration curve was obtained by plotting different concentrations of caffeic acid (0.01–1000 μM) imprinted quartz crystal versus frequency shifts. The detection limit, defined as the concentration of analyte giving frequency shift equivalent to three standard deviation of the blank, plus the net blank frequency shift, was 7.8 nM for MAAP-Fe(III) based nanosensor. The linear range ($y=27.514x+125.2$) was established between 0.0100 and 1000 μM with a coefficient (R^2) of 0.9836. The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. There were no other study about caffeic acid in literature using the MIP-QCM technique. Therefore, it is difficult to compare this result with the literature. However, the detection limit of caffeic acid was found as being 0.11 μM by using liquid chromatography [42].

3.4. Determination of caffeic acid content in plant materials by prepared QCM nanosensor

There are many plant materials which have high content of caffeic acid. For this study to analyse caffeic acid quantity; centaury, sage, black tea, apple and potato are selected. Before the measurement, some pre-treatment steps were applied to selected materials. Solvent extraction method was used to insulate caffeic acid from the selected materials [41]. For this method, each materials were weighed in 5 g and cartridges were prepared with filter paper. These cartridges were placed in Soxlet apparatus and first entreated with dietylether for 9 h to remove impurities such as oil or wax, and then extracted with suitable solvent for 7 h. Solvents were evaporated by using rotary evaporator. The eluent which was obtained after pre-treatment step consisting of caffeic acid was squeezed onto MAAP-Fe based QCM nanosensor. Caffeic acid level in each material was determined by calibration curve using the frequency values.

High pressure liquid chromatography (HPLC, Shimadzu UV–vis dedector) was used for comparison of the analytical performances of the prepared QCM electrode. For this purpose, Perkin Elmer C18 (5 μm, 150 × 4.6 mm) column was used. The amount of caffeic acid in plant samples using both MAAP-Fe based QCM nanosensor and HPLC were given in Table 2. The sensor results were justified by comparative chromatographic measurements.

All measurements were performed three times at 95% confidence level. The accuracy of measurement was checked with standard addition method. It should be noted that although the same nanosensor has been used 18 times by washing with methanol/glacial acetic acid (9:1, v/v), without loosing substantially (only 5%) measurement effect of the nanosensor (Fig. 6).

4. Conclusion

In the present study, by using the molecular imprinting technique with polymerization of metal-chelating monomer (MAAP-Fe) in the presence of template molecule (caffeic acid), a new caffeic acid imprinted QCM nanosensor has been investigated with good reusability, short response time, wide linear range, low detection limit (7.8 nM). The value of Langmuir constant (b) (4.06×10^6) obtained using Langmuir graph shows that the affinity of binding sites is strong. Besides, selectivity experiments demonstrated that the selectivity coefficients of the MAAP-Fe(III)-caffeic acid complex with respect to chlorogenic acid having similar structure with caffeic acid is 22. The prepared QCM nanosensor had a good storage stability and the sensing unit could be regenerated for reuse for long period of time.

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