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Design, synthesis and evaluation of a molecularly imprinted polymer for hollow fiber–solid phase microextraction of chlorogenic acid in medicinal plants

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ABSTRACT

In this study, a simple preparation approach was developed for modified bisphenol A (BPA) molecularly imprinted polymer sorbent used in the hollow fiber solid phase microextraction (MIP-HF-SPME) of chlorogenic acid (CGA). The pre-polymer solution containing the template was introduced into the polypropylene hollow fiber segment for in situ polymerization. MIP-HF-SPME conditions based on the modified MIP-sorbent were optimized. Finally, the tool was used for selective extraction of chlorogenic acid in Echinacea purpurea, a medicinal plant. Main parameters affecting synthesis of organic–inorganic hybrid MIP and microextraction procedure were investigated and optimized. The measurements were done under the optimal conditions. The limit of detection has been gained 0.08 ng/mL. The linear range and relative standard deviation (RSD %) are 0.2–1000 ng/mL and 0.38 (n = 3) respectively. The average relative recoveries of spiked analyte in the four concentration levels were between 84.8 and 97.2%.

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1. Introduction

One of the most important bioactive compounds rich in the leaves of some medicinal plants such as Echinacea purpurea and Eucommia ulmodies is chlorogenic acid (CGA); a member of a family of naturally occurring organic compounds.

CGA is an antioxidant and have important biological properties, the most notable of which is the capacity to act as tumor prevention through activation of protein kinase. Anti-bacterial, phlogistic, mutagenic and other biological activities are some of its medicinal applications [1]. Undoubtedly, biological studies and pharmacological applications need high purity of chlorogenic acid, but there are some difficulties in the extraction and production process of this phenylpropanoid compound. Therefore, pre-concentration methods before analysis, are necessary.

As some similar compounds whose functional groups have similar chemical activities like caffeic acid, gallic acid, protocatechuic acid, vanillic acid, and so on (see Fig. 1) [2], CGA cannot be extracted efficiently by general organic solvents and CGA in many medicinal plants is present in trace and ultra trace amounts making it rather difficult to purify CGA from the leave extracts [3].

Some standard methods have been reported in the determination of CGA based on thin layer chromatography and relative retention time by high performance chromatography methods [3–7].

Recently solid phase microextraction has been developed by using of molecularly imprinted polymers (MIPs) for the selective extraction and pre-concentration of many groups of analytes [8–11]. Scientific reports have shown that extraction yield of MIP-coated SPME fiber has increased significantly [12–14]. Generally, MIPs are synthesized by organic compounds [15], but in case of bio-molecular templates, because of their very little solubility and to minimize the risk of their losing bioactivities in organic solvents, an aqueous imprinting process is obviously much preferred [16,17]. Also inorganic imprinted polymers are naturally fragile in a large area membrane; moreover, it could be difficult to remove of templates in such matrices. A hybrid of organic–inorganic imprinted polymer could be a good solution to above shortcomings [18,19]. Indeed, some beneficial properties of organic–inorganic hybrid MIPs like high flexibility, low density, thermal and mechanical stability, long shelf life and its low cost, as its excellent advantages, could not be disregarded [20,21].

Coupling of sol–gel process with MIPs in some extraction methods has been carried out in recent years [22–24].

Our group has recently introduced a novel SPME technique namely; hollow fiber solid phase microextraction (HF-SPME) in which the sorbent containing a carbon nanotube reinforced [25] nano-composite was prepared via sol–gel technique [26–28]. The sol, after preparation, was injected into a piece of polypropylene hollow fiber and the process of in situ gelation occurred inside the fiber. This new technique was used in hallow fiber

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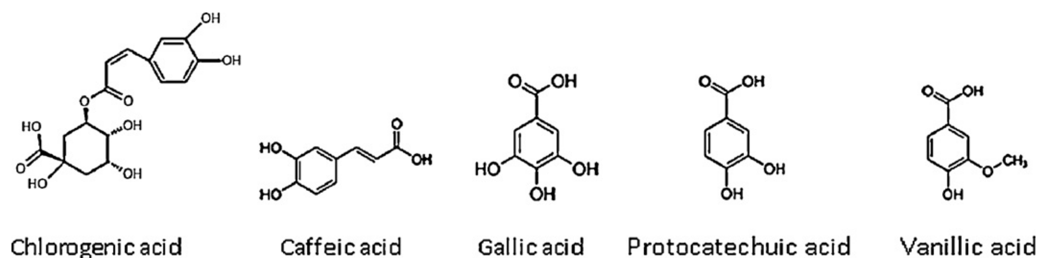

Fig. 1. Some phenylpropanoid compounds whose functional groups have the same chemical activity.

SPME (HF-SPME) to extraction and pre-concentration of some analytes.

The aim of this paper has been to develop the previous studies. In so doing, our efforts have led to the improvement of the selectivity during extraction and/or subsequent clean-up of HF-SPME technique. An acrylate based molecularly imprinted polymer was designed and synthesized via sol–gel technique and combined with functionalized carbon nanotubes (F-MWCNTs). This reinforced monolithic sorbent was used for extraction of trace amounts of chlorogenic acid in natural samples.

Its characteristics, extraction capability and selectivity were investigated as compared with the non-imprinted polymer (NIP) HF-SPME sorbent. The MIP-HF-SPME fiber has been coupled directly with HPLC for simultaneously multi-residue monitoring of chlorogenic acid in real samples.

2. Experimental

2.1. Chemicals and materials

Methacrylic acid (MAA), vinyl triethoxysilane (VTEOS), benzoylperoxide, tetraethyl orthosilicat (TEOS), chlorogenic acid, caffeine, caffeic acid, gallic acid, acetonitrile, methanol, ethanol, chloroform, dichloromethane, hydrochloric acid and phosphoric acid were all purchased from Merck (Schuchardt, Germany). Analytes were analytical grade and solvents all HPLC grade. The hollow fiber polypropylene membranes, Q3/2 Accurel PP (200 μm thick wall, 600 μm inner diameter and 0.2 μm average pore size) were purchased from Membrana (Wuppertal, Germany). The multi-walled carbon nanotubes (MWCNTs) were obtained from the Research Institute of the Petroleum Industry (Tehran, Iran). The mean diameter of the MWCNTs was 10–15 nm, the length was 50–100 nm and purity >98%.

2.2. HPLC apparatus

In this study the HPLC system was a Knauer (Berlin, Zehlendarf, Germany) and consisted of a Knauer (K-2600) UV detector. The column used was Perfectsil Target RP-18 column (4.6 mm diameter, 250 mm length, ODS-3 5 μm) from MZ-Analysentechnik (Wohlerstrabe, Germany). An RP-18 guard column was fitted at the upstream side of the analytical column. The mobile phase consisting of 0.1% (v/v) phosphoric acid in de-ionized water/methanol (80:20 at 15 min run times isocratic mode) was filtered by Milli-Q filtering system and delivered by a Knauer K-1001 HPLC pump. The flow rate of the mobile phase was 1.0 mL/min and the UV detection wavelength was set at 280 nm.

2.3. MIP synthesis

2.3.1. Preparation of organic–inorganic hybrid solution

Two solutions were prepared separately as follows: for organic part of MIP, 20 mmol MAA (functional monomer) was mixed with 18.5 mmol VTEOS (cross-liker) and 0.5 mmol benzoylperoxide (initializer) was added to the mixture at 50 °C and stirred for 20 min. This was labeled solution (A). As inorganic part of the hybrid, 2.7 mL TEOS was mixed with 2.7 mL ethanol for 10 min then 71 mg chlorogenic acid (the template) was added and stirred at 50 °C. Finally 0.8 mL 12.5% (v/v) HCl 37% in de-ionized water was added to the mixture to complete the sol. This mixture was labeled solution (B). Then immediately, before gel formation, 5 mL of solution (A) was added very slowly (in a period of 10 min) to 5 mL of solution (B) and stirred at 40 °C for 1 h.

2.3.2. Carbon nanotubes reinforced molecularly imprinted sol–gel materials (MISGMs)

20 mg of MWCNT which had been acid functionalized [25] was added to the above solution gradually. Then the mixture was put in ultrasonic bath for 2 h. After sonication a black homogeneous solution was emerged.

2.4. Fiber treatment

The polypropylene hollow fiber was cut into small segments with a length of 2.5 cm each. 12 μL of the dispersed mixture was injected into the fiber segments gradually using a micro-syringe. The top and bottom of the segments were closed by a nylon string to prevent of leakage. The fiber was left for 72 h till the gel network was formed in situ. To evaluate the effect of F-MWCNTs on the extraction, the process was first conducted by adding F-MWCNTs and then repeated without it.

2.4.1. Preparation of MIP and NIP fibers

After gelation, at 40 °C and for 10 min each treated fiber segment was put in a glass vial and subjected to 2 mL methanol in de-ionized water 95% (v/v) as the removal solvent to remove the entrapped template. The MIP fibers were obtained after drying under air exposure. The scanning electron micrograph image of the MIP-fiber is shown in Fig. 2.

Non-imprinted polymer (NIP) control fibers were prepared and treated in the absence of chlorogenic acid in the same manner described above.

2.5. MIP assisted HF-SPME procedure

The already prepared fiber segment was submerged in the sample solution containing 5.0 mL of chlorogenic acid 0.1 μg/mL in a suitable vial. The vial was covered and stirred at 700 rpm for 20 min. Uptake of the analyte was carried out after extraction by submerging of the fiber into 2.0 mL methanol 95% (v/v) in de-ionized water for 10 min at 40 °C on the hotplate-stirrer. 40 μL of the methanolic phase containing desorbed chlorogenic acid was injected into the HPLC for further analysis.

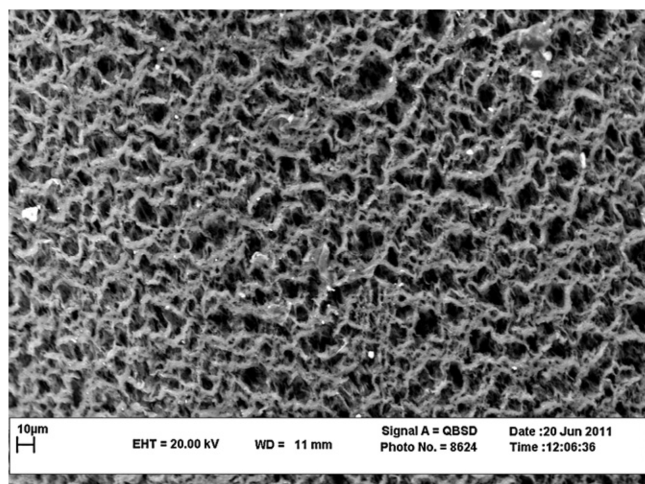

Fig. 2. The scanning electron micrographs images of the MIP-fiber under the magnifications of 1000.

3. Results and discussion

3.1. Characterizations of the organic–inorganic hybrid MIP-HF-SPME fiber

MIP synthesis conditions were strongly influential on the HF-SPME procedure. Therefore, essential conditions were studied and optimized carefully.

3.2. Effect of functional monomer concentration

The ratio of functional monomer to cross-linker was examined in this study. This ratio was determined by a comparison of HPLC chromatograms of the various mixtures of two compounds. As shown in Fig. 3 the best ratio concentration of MAA to VTEOS was obtained at 1.08. So, 20 mmol of MAA was used per 18.5 mmol VTEOS in the reaction.

3.3. Amount of template

Molar ratio of the template to the functional monomer must be optimized. Fig. 4 shows that, the best adsorption was obtained by 0.01 ratio of template to monomer. To do this, 71 mg (0.2 mmol) chlorogenic acid versus 172.12 mg (20 mmol MAA) was used in the formation of the MIP.

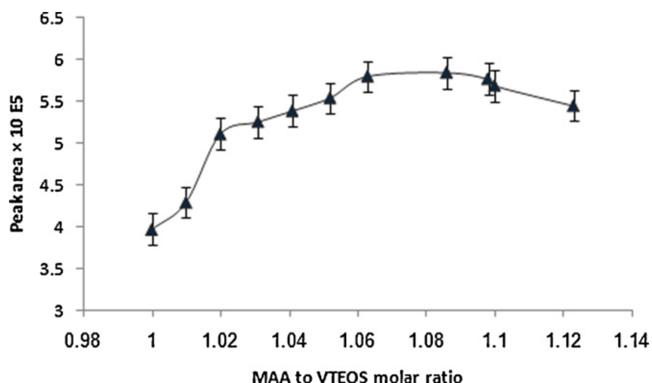

Fig. 3. Influence of MAA to VTEOS ratio in preparation of Imprinted polymer. Extraction Conditions: length of fiber segments, 2.5 cm; volume of donor phase, 5 mL; extraction time, 20 min; stirring rate, 700 rpm, pH of sample, 3.9.

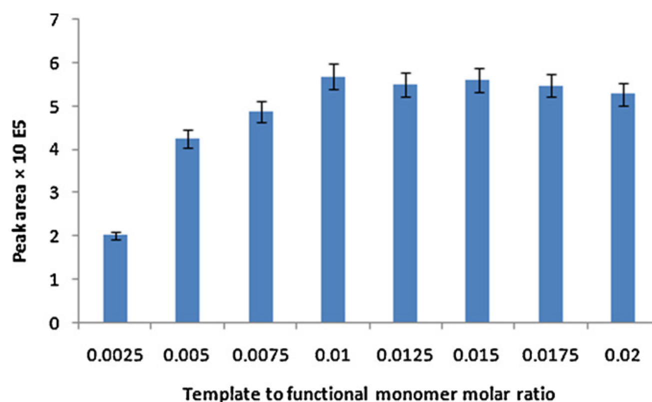

Fig. 4. The effect of molar ratios between template and functional monomer in MIP membrane. Extraction Conditions: length of fiber segments, 2.5 cm; volume of donor phase, 5 mL; extraction time, 20 min; stirring rate, 700 rpm; pH of sample, 3.9.

3.4. Organic–inorganic solutions ratio

According to the technique for the hybrid of (A) and (B) solutions, the amount of two solutions should be optimized for the best adsorption efficiency. Although the two solutions were prepared separately, the ratio of solution (A) to solution (B) could affect the final sorption performance. This encouraged us to optimize the (A) to (B) solutions ratio. Based on the experimental results in subsequent experiments we used (A) and (B) solutions volumes with the 1:1 ratio.

3.5. Effect of MWCNTs concentration

Carbon nanotubes in MIP can help mass transfer dramatically. The amount of MWCNTs in range 0–8 mg/mL was studied and the best result was obtained in 2 mg MWCNTs per each mL of the mixed solution.

3.6. Optimization of the HF-SPME conditions

In this modified HF-SPME method, some effective parameters should be optimized in order to achieve the best efficiency. Optimization was entirely carried out on aqueous chlorogenic acid solution 0.1 μg/mL as the analyte. Evaluation of the extraction parameters in different conditions was carried out using HPLC peaks area which indicated the analyte concentration.

3.6.1. Donor to acceptor volume ratio

Based on the previous works, hollow fiber segments with 2.5 cm length were used in this study [8]. Therefore, optimization of donor to acceptor phase ratios was carried out only with different volumes of donor phase. Optimal volume of donor phase was obtained 5 mL.

3.6.2. Effect of extraction time

As expected, the extracts obtained in this technique increased with the increase of extraction time. This is because due to longer solid–liquid contact time more solute can be extracted.

This conclusion was then verified by the experimental data obtained from extraction of analyte, while extraction time was varied from 5 to 40 min. The result of this experiment is presented in Fig. 5. It was found that extraction rate was very rapid in the beginning of the extraction process due to the large mass transfer driving force, namely the difference of solute concentration at the solid and liquid phase. However, prolonged extraction time resulted in the reduction of extraction rate due to the reduction of mass transfer driving force. There was no significant increase of extraction after

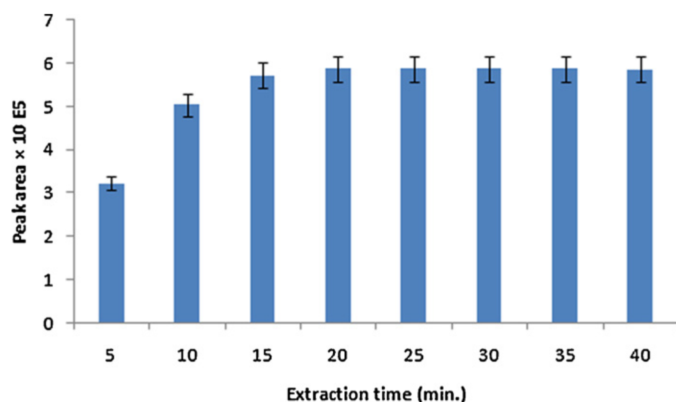

Fig. 5. Optimization of extraction time. Extraction Conditions: length of fiber segments, 2.5 cm; volume of donor phase, 5 mL; extraction time, 20 min; stirring rate, 700 rpm; pH of sample, 3.9.

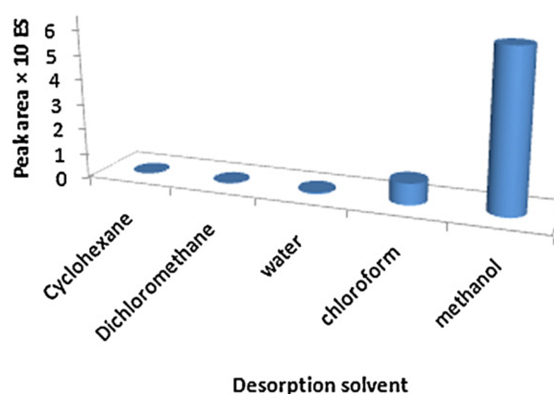

Fig. 6. Optimization of back-extraction solvent. Extraction Conditions: length of fiber segments, 2.5 cm; volume of donor phase, 5 mL; extraction time, 20 min; stirring rate, 700 rpm; pH of sample, 3.9.

20 min of extraction time and for further experiments the same time span was applied.

3.6.3. Effect of the stirring rate

Stirring provides fresh donor solution for the sorbent to extract analyte and reduces the effect of the stationary boundary layer zone (Nernestian layer) produced close to the acceptor phase; these factors promote analyte transport from the donor phase to the acceptor phase.

The results revealed that the peak area of analyte increased with increasing stirring speed up to 700 rpm.

This result indicated the positive effect of agitation on the mass transfer coefficient. On the other hand, further agitation speed may also cause lower extraction efficiency because hollow fiber was vibrated by the surrounding flow and air bubbles reduced contact area between analyte and sorbent. These factors led to a decrease in the precision of the method [29].

3.6.4. Effect of pH on the extraction

It is well known that pH of the donor phase in microextraction method depends on the type of the analyte. For the best result, the pH of donor was adjusted close to pK_a forming molecular analyte. The pH was tested for donor phase in the ranges between 1 and 7 according to its acidic properties. Consequently, the highest extraction efficiency for chlorogenic acid was found at pH 3.9, and we used this pH for further analyte extraction processes.

3.7. Optimization of template removal and desorption conditions

All SPME fibers need the extracted analyte desorption by some specified methods. In this research removing the template and desorption of the analyte were carried out by solvent washing assisted by a heating shock and ultrasound application. Thus different solvents in a wide range of polarity, desorption temperatures, and the time of sonification were studied and optimized.

3.7.1. Solvent selection

Molecular structure and polarity have a key role in the selection of solvent in the removal the template in MIPs or desorption of the analyte. Chlorogenic acid is a relatively polar compound with a large molecular structure which seems to dissolve in a polar solvent better than in a non-polar one. Five solvents including cyclohexane, dichloromethane, chloroform, methanol and water were used as the template removal solvent and analyte desorption solvent in the back extraction step. According to the experiments (Fig. 6), methanol provides acceptable result as a washing solvent in removing and desorption roles.

3.7.2. Effect of desorption temperature

To obtain the best efficiency, after microextraction of analyte we applied simultaneous heating and washing solvent (as two effective factor) to remove template and for desorption of anlayte. Optimized desorption temperature of this process was obtained in 40 °C for methanol. This is lower than the boiling point of methanol.

This optimization accomplished in the range 25–55 °C and for other experiments we used 40 °C as the best back-extraction and the template removing temperature.

3.7.3. Effect of ultrasonic agitating duration time

To obtain a high efficiency factor of microextraction using the designed membrane, removal of the template and desorption of the analyte were assisted by ultrasound agitation besides of the washing solvent. This was applied by an ultrasonic bath for between 2 and 22 min, as agitation time. For both steps the best result was obtained after 10 min of ultrasonic agitation. There was no significant difference between the results with more agitation time duration.

It is noteworthy that in order to remove the template molecule from MIP membrane and desorption of the analyte from sorbent fiber three factors including solvent, heating and ultrasonic agitation were applied simultaneously and as the result most efficient parameters were obtained.

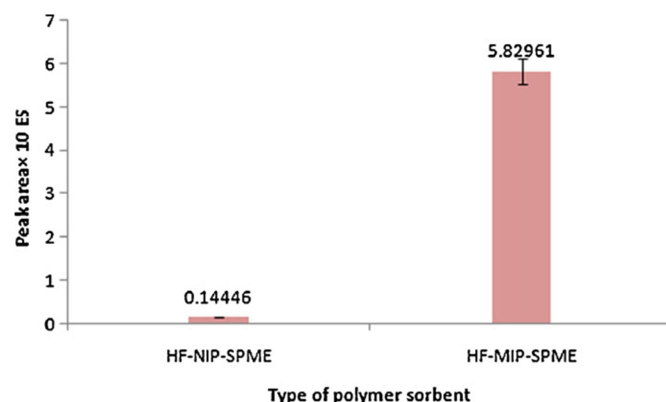

Fig. 7. HF-SPME of chlorogenic acid by NIP and MIP, under the optimal conditions. Analyte concentration, 100 ng/mL.

Table 1
Selectivity of the membrane for chlorogenic acid as the analyte.

	Substance			
	Chlorogenic acid[a]	Gallic acid[b]	Caffeic acid[b]	Caffein[b]
Recovery %[c]	93.9	3.7	Below detection limit	11.4

[a] As the analyte.
[b] As interference substance
[c] Recovery was calculated for a 1 μg/m solution of each substance.

Table 2
Relative recovery and RSD% of MIP-HF-SPME technique for chlorogenic in the Echinacea purpurea sample.

Spiked analyte (ng/mL)	Relative recovery %	RSD% within day ($n=3$)	RSD% with day ($n=9$)
0.5	88.5	2.41	5.78
10	92.6	0.32	0.95
50	84.8	1.73	2.05
100	89.9	0.38	1.21
500	97.2	2.61	6.82

3.8. Analytical consideration of the method

3.8.1. Selectivity of the membrane

Insertion of F-MWCNTs into the hybrid MIP led to analyte sorption capacities reaching maximum level. Moreover, mixing of organic–inorganic causes a high selectivity and adsorption capacity for the method. As shown in Table 1, the best result was carried out by chlorogenic acid as the analyte than other substances like caffeic acid, gallic acid and caffeine.

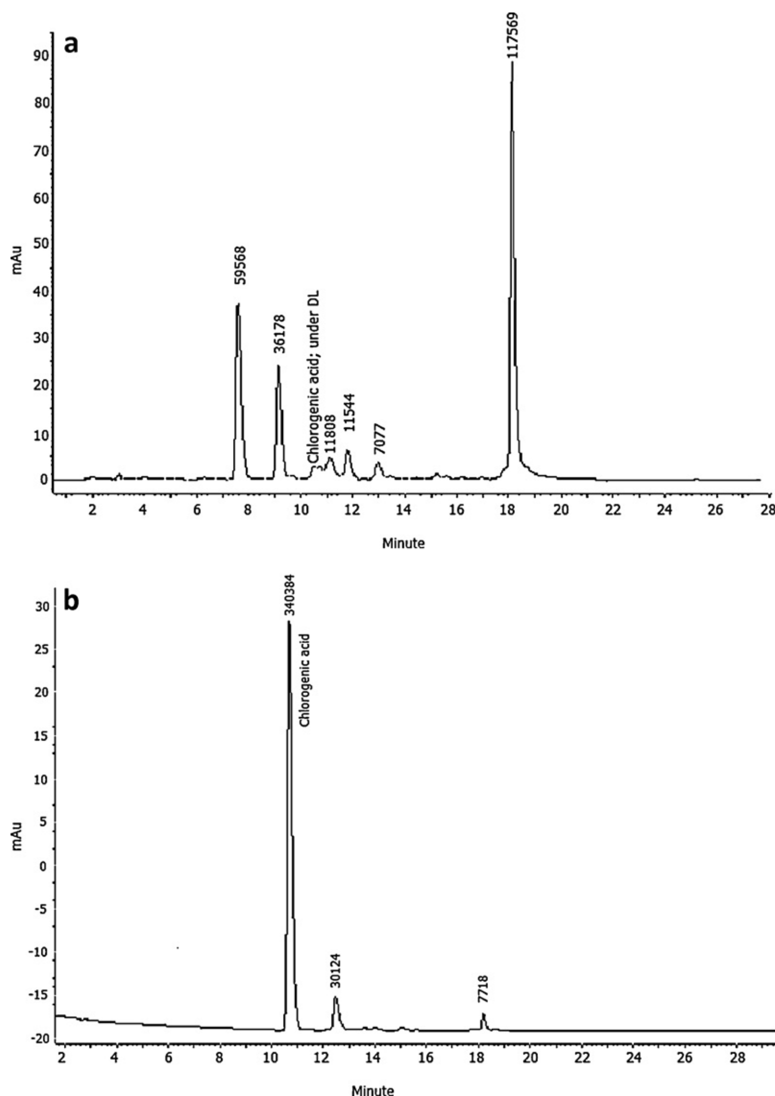

Fig. 8. HPLC Chromatogram of chlorogenic acid in herbal extract: (a) before MIP-HF-SPME and (b) after MIP-HF-SPME. HPLC conditions: isocratic mode, mobile phase consisting of 0.1% (v/v) phosphoric acid in de-ionized water/methanol, flow rate 1.0 mL/min, detection wavelength 280 nm.

Table 3
Amount of chlorogenic acid in some natural product of Echinacea Purpurea (as a medicinal plant) by MIP-HF-SPME technique.

Product name	Producing countries	Drug format	Chlorogenic acid[a]
Immunosupport	Iran	Drops	0.51 ng/mL
Echinaforce	Germany	Drops	1.28 ng/mL
Echinaherb	Germany	Drops	1.70 ng/mL
Echinacea Stada	Germany	Drops	3.4 ng/mL
Echinacea Natriva	Canada	Capsules	0.41 mg g^{-1}
Echinacea Nature Source	Canada	Capsules	0.61 mg g^{-1}

[a] Chlorogenic acid amount not indicated in product packaging.

To better characterize the method selectivity chlorogenic acid (100 ng/mL) was extracted under the optimal conditions with MIP and NIP polymer sorbent separately and the results are shown in Fig. 7. This efficient uptake of the main analyte by the synthesized MIP was acceptable and selectivity of the method was at a desired level.

3.8.2. Performance of the method

The analytical parameters of this technique, such as linearity, limits of detection and quantification, relative standard deviations (RSD), extraction efficiencies and pre-concentration factors for chlorogenic acid as analyte were examined. The linearity is ideal in the dynamic wide range (0.2–1000 ng/mL) for chlorogenic acid. For this compound, LODs is 0.08 ng/mL and RSD% ($n = 3$) is 0.38. The good correlation coefficient, 0.997 with the equation $y = 0.0678x - 0.028$ and low detection limit as well as wide LDRs are the other advantages of this technique.

HF-SPME is not exhaustive extraction method, so the relative recovery was determined as the ratio of the chlorogenic acid concentration founded in Echinacea purpurea extract and standard sample, with both samples spiked at the same concentration level (1.0 ng/mL).

The repeatability (three samples in one day) and reproducibility (nine samples in three consecutive days) in triplicate analysis (each day) were tested on environmental samples. The results are depicted in Table 2. The pre-concentration factor of 4145 ($n = 3$) was determined experimentally from result of deviation of the analyte peak area with the same concentration after and before the extraction multiple dilution factor.

A hydro-alcoholic extract of Echinacea purpurea named Immunosupport (a product from an Iranian pharmaceutical company) as a natural sample was tested by this analytical method. Results of the analysis determined 0.51 ng/mL chlorogenic acid in the medicinal sample (Fig. 8).

Table 3 shows amount of chlorogenic acid in some other herbal product determined by the presented technique.

In this manner determination of chlorogenic acid is possible in diluted hydro-alcoholic extract which is used as precursor of herbal drags. This technique could also be developed for other chemical important substances such as polyphenols, flavonoids, alkamids and so on in phytochemical studies.

4. Conclusion

The molecularly imprinted materials prepared via sol–gel process have a great potential for various analytes assay applications. The interesting area of sol–gel combined with molecular imprinting provides a new route for the improvement of the conventional MIPs properties and in identifying new applications of imprinted polymers. Ongoing research needs to be directed at enhancing selectivity of sol–gel polymeric matrix for successful imprinting of the biological acids and other molecules that contain more homogeneous binding sites, have a higher affinity for the target analyte and can be routinely prepared and used in aqueous systems. In the present work, the use of MIPs in the novel HF-SPME is described.

The combination of molecular imprinting and HF-SPME technique provides a powerful sample preparation tool in terms of selectivity, simplicity, and flexibility. This research reports a novel molecularly imprinted polymer (MIP) sorbent with chlorogenic acid as template by improved multiple co-polymerization method. The obtained SPME device exhibits excellent characteristics such as high porosity and chemical stability. Extraction performance shows that the MIP-HF-SPME has stronger affinity to the template molecule and the control polymer-sorbent without addition of template. The extraction effective variables were investigated. The MIP-HF-SPME fiber demonstrated its efficiency for extraction of chlorogenic acid in medicinal samples.

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