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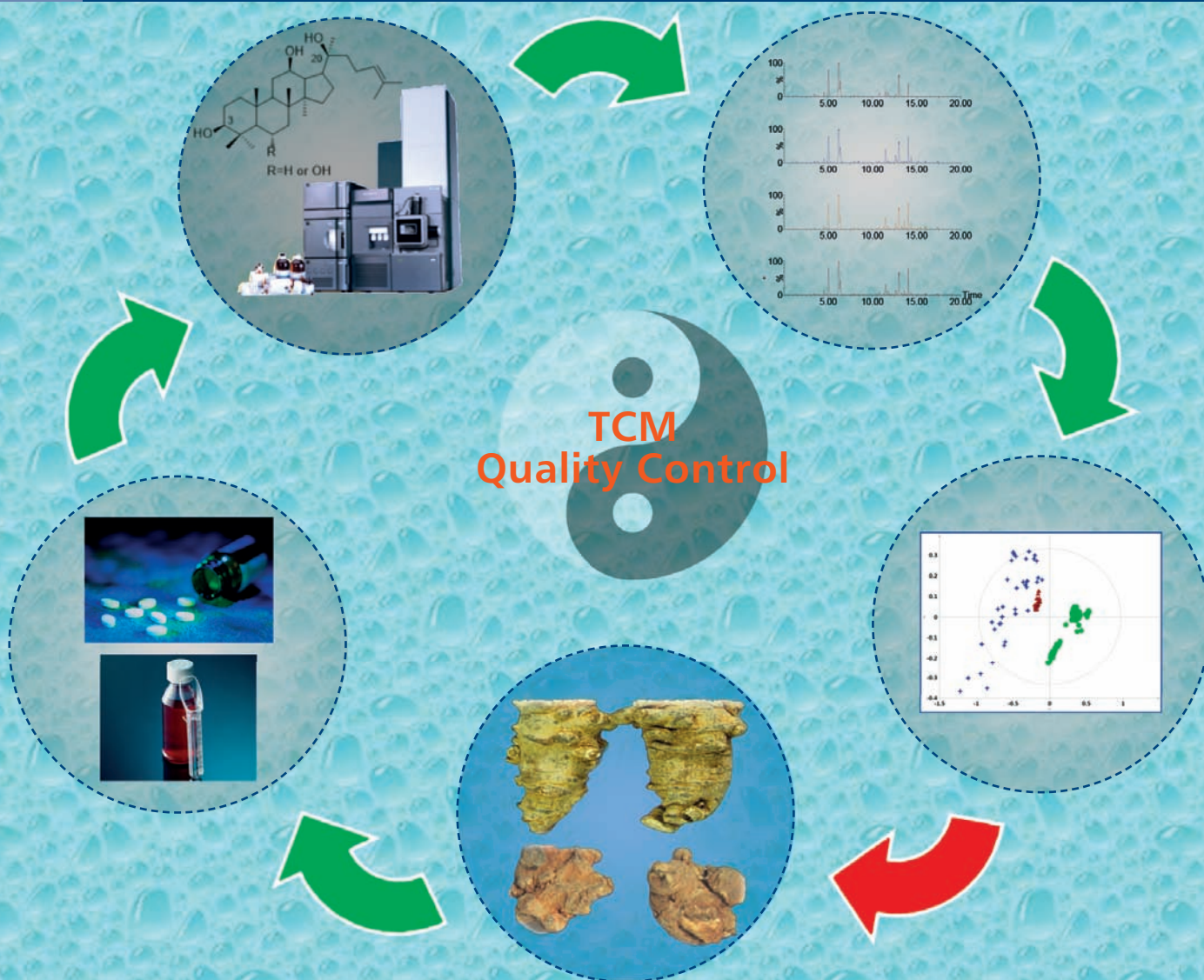
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RESEARCH ARTICLE

Synthesis of a molecularly imprinted polymer for the selective recognition of carmoisine (Azorubin E122) from pomegranate juice

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Since natural pigments are lost during the processing of beverages such as pomegranate juice, carmoisine, as an adulterant, is often added into the pure juice to improve color characteristics. In this study, molecularly imprinted polymers, as an adsorbent of carmoisine, were synthesized using acrylamide, methacrylic acid, and 4-vinylpyridine as functional monomers and then they were evaluated in terms of the separation and detection of carmoisine. Experiments on the batch adsorption of carmoisine 10 ppm stock solution revealed a better binding capacity for the 4-vinylpyridine-based polymer in comparison to methacrylic acid and acrylamide polymers. The complexation of carmoisine with the 4-vinylpyridine-based polymer was confirmed by Fourier transform infrared spectroscopy. The synthesized polymer exerted a high thermal degradation point and average diameter of polymer particles were obtained to be 0.2 µm by dynamic light scattering analysis. This work showed that detection of pomegranate juice adulteration with carmoisine is not necessarily difficult, time consuming or expensive with selective separation techniques such as molecularly imprinted polymers.

KEYWORDS

carmoisine, molecularly imprinted polymers, pomegranate juice, 4-vinylpyridine

1 | INTRODUCTION

Carmoisine is a synthetic azo dye usually found as a food additive in beverages, candies, jam, jelly products, instant puddings and so on. Synthetic dyes improve the appearance of foods and they are stable in food processing conditions such as different ranges of pH and high temperature in addition to being stable when exposed to light and oxygen. Azo dyes are characterized by the presence of chromophoric azo group (–N=N–) attached to the substituents, mainly benzene or naphthalene derivatives containing electron withdrawing or donating groups or both [1]. Azo dyes may cause harmful effects in the body and allergic and/or intolerance reactions, particularly among those with an aspirin intolerance and asthmatics [2]. Due to the loss of natural dyes during processing of beverages such as pomegranate and red grape juice, carmoisine is often added into the pure juice to adjust the color, which is a type of adulteration in industries. Accordingly, developing a fast, selective and accurate analytical technique to detect this type of adulteration by synthetic dyes in fruit juices is needed. Several analytical techniques have been established for carmoisine detection in food products. Spectrophotometry techniques including UV-vis [3] and FTIR [1,4] as common methods as well as Raman [1], differential pulse polarography [5,6], and HPLC [7] have been reported.

These methods have various disadvantages such as high cost, insufficient selectivity, time consuming, and hard sample preparation [8]. A new method capable of obviating these disadvantages, molecularly imprinted polymer (MIP) technology provides the synthetic polymer with a specific cavity matching with a target molecule. High affinity, selectivity, stability, and simplicity of preparation are among several advantages of MIPs [9,10]. MIPs are also stable at extreme pH values, organic solvents, and temperatures, which allows for more flexibility in the analytical methods [11,12]. These properties demonstrate the potential of MIPs for being

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Abbreviations: AA, acrylamide; AIBN, 2,2 azobis isobutyronitrile; EGDMA, ethylene glycol dimethacrylate; MAA, methacrylic acid; MIP, molecular imprinting polymer; NIP, nonimprinted polymer; PDI, polydispersity index; TGA, thermogravimetric analysis; 4-VP, 4-vinylpyridine

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utilized as adsorbents in sensors, antibody receptor mimics, and SPE [13].

This method involves radical polymerization of functional monomers with the target molecule by covalent or noncovalent interactions and then arrangement of monomers using a cross-linking agent. After the template is eluted by chemical reaction or extraction, specific binding sites are created that are complementary to the template in size, shape, and position of the functional groups [8,9]. Several variables including monomer type and amount, cross-linker, initiator, and solvent amount affect the final characteristics of MIPs regarding capacity, affinity, and selectivity for the target molecule. Several studies have considered MIP preparation for detection of synthetic dyes (Table 1).

In comparison to these studies, this work was mainly focused on fabricating a facile MIP with a variety of monomers for separation of carmoisine from pomegranate juice. Precipitation polymerization, which is performed in a more dilute polymerization mixture and gives submicron-sized polymers in comparison to other techniques [11,12], was applied as polymerization method in this study. The potential of imprinted polymers in carmoisine separation and detection was investigated by HPLC, FTIR, thermogravimetric, and particle size analysis methods.

2 | MATERIALS AND METHODS

2.1 | Reagents, solutions, and apparatus

All polymerization reagents containing methacrylic acid (MAA), acrylamide (AA), ethylene glycol dimethacrylate (EGDMA), 2,2-azobisisobutyronitrile, ammonia 25% and HPLC-grade acetonitrile and methanol were provided by Merck (Germany) and the template carmoisine (also called azorubine, E122), 4-vinylpyridine (4-VP) and ammonium acetate were purchased from Sigma–Aldrich (Spain). Methanol (CH_3OH) as a washing solvent was purchased from Scharlau. Double distilled water and deionized water were used in the preparation of all solutions and in all experiments.

Devices applied in this study were: Centrifuge (Hettich, eba 270, Germany), ultrasonic equipment (Ultrasonic cleaner, Parasonic 2600s, Iran), micro centrifuge (Eppendorf, MiniSpin, Germany), laboratory balance (Acculab sartorius group, Atilon, USA), magnetic heater-stirrer (Heidolph, mr hei-standard, Germany), HPLC (CECIL, CE4900, UK), FTIR spectrometer (Perkin Elmer, Spectrum Two, USA), oven (Memmert, EFB 400, Germany), deionizer (Millipore, Direct Q UV-3, France), horizontal tube shaker (Behdad, Iran), particle size analyzer (Malvern Zetasizer, Nano-ZS, UK), scanning electron microscope (Zeiss, LEO 1430VP, Germany) and thermogravimetric analyzer (Linseis, STA PT-1000, Germany).

2.2 | Carmoisine-imprinted polymer synthesis through precipitation polymerization

A total of 0.1 mmol template, carmoisine, was added into a 100 mL flask containing 10 mL acetonitrile/methanol (80:20) as a porogen solvent and was mixed by sonication until complete dissolution.

Monomers (MAA or AA or 4-VP) at 0.4 mmol were added and kept for 12 h for prepolymerization under stirring. Cross-linker (EGDMA) at 2 mmol and initiator (2,2-azobisisobutyronitrile) at 30 mg were then added to prepolymerized mixture. After sonication for 5 min, degassing of the mixture was done by purging N_2 for 10 min and then the container was sealed completely. Polymerization started by heating the mixture to 60°C in a hot water bath. After 24 h, the obtained solid polymer was washed with methanol/ammonia (90:10) in Soxhlet extraction system, until no carmoisine was detected in the supernatant and then was washed three times with deionized water to elute methanol/ammonia from the polymer. This stage was crucial in MIP synthesis since incomplete rinsing of the template makes its rebinding into the polymer interaction sites difficult. Drying of the solid polymers was performed at 55°C in an oven for 24 h, then it was ground carefully and sieved. Nonimprinted polymer (NIP) as a control polymer was also prepared following the same procedure as MIP in the absence of carmoisine.

2.3 | Binding test of the synthesized polymers through HPLC

First, 20 ppm carmoisine stock solution was prepared with deionized water. Batch binding test has been developed to evaluate the binding capacity of imprinted polymers toward carmoisine. For binding test, 10 mg of MIP or NIP and 4 mL carmoisine stock solution (0.5, 2.5, 10, and 20 ppm) was mixed in a 10 mL tube and then it was horizontally stirred at 200 RPM for 5 min to achieve an equilibrium between polymer and template. Each solution was prepared three times. The mixture was then centrifuged at 10 000 RPM for 10 min. After syringe filtering (PTFE, 0.22 μm) of the supernatant, the concentration of free carmoisine was analyzed by HPLC–UV. The amount of carmoisine adsorbed to the binding sites of the polymer was obtained by subtracting its initial concentration from the concentration of free carmoisine in the supernatant. Adsorption capacity of carmoisine imprinted polymer was calculated according to Eq. (1):

$$Q = (C_i - C_f) \times V/m \tag{1}$$

where V is the solution volume (L); m is the polymer mass (g) and C_i and C_f are the initial and final (supernatant) carmoisine concentrations in the binding medium (ppm), respectively [14].

TABLE 1 Different MIP preparation approaches for synthetic dyes

Template (mmol) [T]	Functional monomer (mmol) [M]	Cross-linker (mmol) [C]	Initiator (mg)	Progen solvent (ml)	Method	T:M:C ratio	Researchers
Tartrazine, 1	AA, 2	N,N'-methylene-bisacrylamide, 10	Potassium persulfate, 0.185	Water, 40	Precipitation	1:2:10	Arabzadeh et al. 2015 [2]; Yaripour et al. 2016 [26]
Sunset yellow, 0.5	MAA 4-VP 1MA3AlBr, 2	EGDMA, 10	AIBN, 60	Methanol: water 4;1, 50	–	1:4:20	Zhao et al. 2014 [13]
Fancy red, 0.1	4-VP, 0.4	EGDMA, 2	AIBN, 20	Aqueous acetonitrile, 10	Precipitation	1:4:20	Long et al. 2009 [19]
Amaranth; Tartrazine; Sunset yellow; Rhodamine, 0.33	MAA, 3.2	EGDMA, 12.8	AIBN, 52.54	Ethanol:glyc 3:1, 40	–	1:10:40	Long et al. 2014 [20]
Chloro-Sudan, 0.5	N,N-dimethylaminoethyl methacrylate, 3.5	EGDMA, 25	AIBN, 0.6	Chloroform, 7.5	Suspension	1:7:50	Baggiani et al. 2009 [21]
Rhodamin B, 0.5	AA, 3	EGDMA, 15	AIBN, 100	Acetonitrile, –	Precipitation	1:6:30	Li et al. 2012 [22]
Sunset yellow, 0.5	2-(Methacryloyloxy)ethyl]trimethylammonium chloride, 2	EGDMA, 5	AIBN, 30	Methanol: water4:1, 50	Precipitation	1:4:10	Zhang et al. 2016 [23]
Sudan 1, 0.1	2-VP, 0.4	EGDMA, 2	AIBN, 30	Acetonitrile, 25	–	1:4:20	Zhao et al. 2010 [24]
Tartrazine, 1	4-VP, 4	EGDMA, 20	AIBN, 0.16mmol	Methanol: water4:1, 100	Precipitation	1:4:20	Zhao et al. 2014 [25]

AIBN, 2, 2 azobis isobutyronitrile

Distribution (k_d) coefficients were calculated by the following equation:

$$k_d = (C_i - C_f) / C_f \times V / m \qquad (2)$$

Imprinting factors of the polymers were obtained as the ratio of $k_{d\,MIP}$ to $k_{d\,NIP}$:

$$IF = k_{d\,MIP} / k_{d\,NIP} \qquad (3)$$

HPLC conditions applied for carmoisine detection were as follows: C_{18} Hichrom 250 mm × 4.6 mm × 5 μm column, methanol/acetonitrile (80:20), and ammonium acetate 1% in a ratio of 60:40 as mobile phase with the flow rate of 1 mL/min, UV detector at wavelength of 515 nm and water/methanol as washing solution [7].

Carmoisine peaks were evaluated by their retention times while comparing the sample and standard spectra that were obtained at 4.56 min. Quantification and linearity ranges of carmoisine were obtained using a standard curve with 14 points. Calibration curve was linear ($A = 541.9\,C + 6.561$; A, absorbance and C, concentration of carmoisine in mg/L) over the range 0.05–50 mg/ L. The square of the correlation coefficient (R^2) was obtained as 0.999. Likewise, the LOD (S/N = 3) and the RSD% ($n = 6$, $C = 5$ mg/L) were 0.015 mg/L and 6.5%, respectively.

2.4 | Selectivity study

Selectivity test was performed as mentioned in binding test. In this way, 30 mg polymer and 4 mL carmoisine, sunset yellow and ponceau red solution (10 ppm) were mixed in a 10 mL tube and were horizontally stirred at 200 rpm for 5 min to achieve an equilibrium between polymer and template. The mixture was then centrifuged at 10 000 rpm for 10 min. After syringe filtering (PTFE, 0.22 μm) of the supernatant, the free concentration of each dye in binding solution was analyzed by HPLC–UV. Adsorbed amount of dyes to binding sites of polymer was obtained from subtraction of initial concentration and free concentration in the supernatant. Selectivity (k) coefficient was calculated by the following equation:

$$k = k_{d(carmoisine)} / k_{d(competing molecules)} \qquad (4)$$

Anthocyanins are the compounds responsible for the red color of pomegranate juice. Anthocyanins are the mono and diglycosylated forms of anthocyanidins with substitutions at the 3 and 5 positions. However, carmoisine as an azo dye has more similarity in structure with other azo group synthetic dyes such as sunset yellow and ponceau red. That is why these dyes have been selected for selectivity test.

2.5 | Spectroscopic analysis

FTIR spectroscopy was used to analyze the molecular structure of the MIP. Hence, the spectra of MIP before and after template elution, carmoisine and 4-VP were recorded by FTIR spectrometer. Before any sample scanning, the KBr spectrum was obtained as a control. For preparation of the samples for FTIR spectroscopic analysis, 1 mg of truly dried sample was mixed with about 150 mg of dry KBr [15]. Thin pellet of each one was prepared by compressing the mixture under about 60 kPa within 10 min in a compress instrument. FTIR spectroscopy was run at a wavenumber ranging from 400 to 4000 cm^{-1} with a resolution of 0.5 cm^{-1}.

2.6 | Particle size and zeta potential analysis

Particle size of the synthesized polymer (diameter and width) was determined by dynamic light scattering technique measuring the random changes in the intensity of the light scattered from a suspension or solution. Both particle size and zeta potential experiments were performed in Zetasizer. Deionized water was used for dispersing the polymer particles. About 10 mg dried powder was diluted with 1 mL dispersing solvent. After sonication and filtration, the suspension was poured in a cuvette for analyses.

2.7 | Surface morphological analysis of polymer

SEM was applied to investigate shape and surface morphology of the polymer. The particles were coated by gold for a few minutes before SEM analysis. SEM measurement was conducted at an accelerating voltage of 20 kV.

2.8 | Thermogravimetric analysis

Thermogravimetric analysis (TGA) measures the amount of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. Approximately, 10 mg of sample was heated at a constant rate of 10°C/min in a thermal range between 0 and 700°C. Before scanning the changes, the atmosphere was made inert by purging nitrogen gas.

2.9 | Pomegranate juice medium

Fruit juice sample was diluted four times with deionized water. Matrix of pomegranate juice and carmoisine with the concentration of 10 ppm was made manually. An aliquot of 4 mL matrix medium was added to 10 mg MIP or NIP and was then stirred horizontally at 200 rpm for 5 min. The mixture was then centrifuged at 10 000 rpm for 10 min and the supernatant was filtered through a 0.22 μm membrane to remove any particulate and was immediately injected into separation system.

TABLE 2 Adsorption amount and performance evaluation of the polymers synthesized by different monomers

Applied monomer in MIP synthesis	Adsorption amount in stock solution (20 mg/L) (%)	LOD (mg/L)	LOQ (mg/L)	Linearity rang	R^2	RSD	Imprinted factor (IF)
4-VP	75	0.015	0.05	0.05-50	0.999	6.5	150
AA	6	0.17	0.5	0.5-25	0.987	7.1	2.5
MAA	trace	–	–	–		–	–
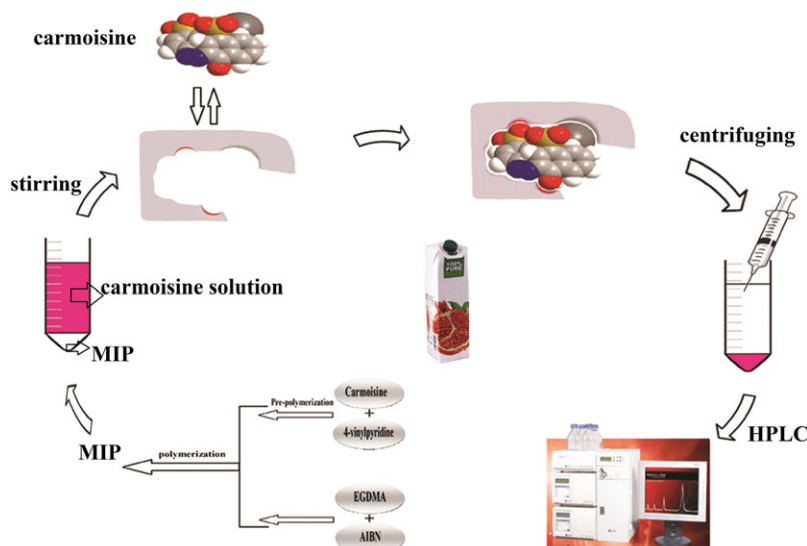
FIGURE 1 Schematic presentation of carmoisine, 4-VP and EGDMA complexation by polymerization and binding test steps (ChemBioDraw Ultra 12.0, Adobe Photoshop CS6)

3 | RESULTS AND DISCUSSION

3.1 | Binding experiment

HPLC was used to evaluate the adsorption capacity of MIP indicating the effectiveness of imprinting process. The HPLC results revealed that 4-VP-based polymers presented higher binding capacity toward carmoisine in comparison to the MAA- and AA-based polymers (Table 2). It was reported that VP monomers were preferred for interaction with templates bearing aromatic rings.

4-VP-based polymer showed the adsorbed amount of 75% for 20 ppm carmoisine solution and 100% for 10, 2.5, and 0.5 ppm carmoisine solutions during 5 min. Considering these data, adsorption capacity of 10 mg 4-VP-based MIP toward carmoisine in 4 mL 20 ppm stock solution, calculated from Eq. (1), was obtained to be 8 mg carmoisine adsorption per gram of synthesized MIP. Schematic presentation of carmoisine, 4-VP, and EGDMA complexations by polymerization and binding test are shown in Fig. 1.

Primary studies showed that adsorption of carmoisine to polymer binding sites had occurred in a few minutes and increasing time intervals did not change adsorption amount.

Rebinding test for evaluating the rebound amount of carmoisine toward the polymer showed that the synthesized MIP polymer could be reused at least six times.

3.2 | Selectivity study

Selectivity test was applied to evaluate the synthesized polymer's ability in selective separation of carmoisine. For this purpose, two synthetic dyes that are analogue in their structure named sunset yellow and ponceau red were chosen. Synthesized 4-VP MIP gave the best binding capacity to carmoisine compared to sunset yellow and ponceau red. According to HPLC results 100, 15, and 4% adsorption were obtained for carmoisine, sunset yellow, and ponceau red, respectively. The distribution coefficient (k_d) values of carmoisine, sunset yellow, and ponceau red were 13.2, 1.86. and 0.53 mL/mg for carmoisine MIP, respectively. The values of selectivity (k) were 7.09 for sunset yellow and 24.9 for ponceau red that could be due to more structural resemblance of sunset yellow to carmoisine than that of ponceau red. The results of distribution and selectivity coefficients showed the size and shape selective properties of synthesized polymer toward carmoisine.

3.3 | Application of synthesized polymer in carmoisine separation from pomegranate juice medium

To investigate the separation potential of carmoisine imprinted polymer from the real medium, the prepared 4-VP MIP was incubated in diluted natural pomegranate juice (dilution factor = 4) with manually added carmoisine in
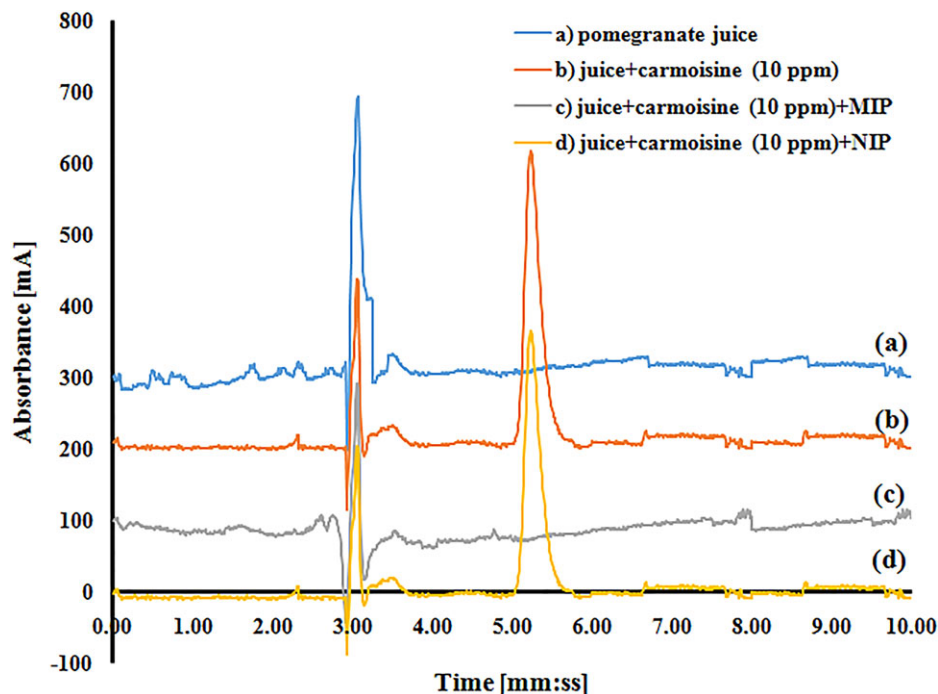
FIGURE 2 HPLC chromatograms obtained for pomegranate juice, juice containing carmoisine 10 ppm and juice + carmoisine + MIP
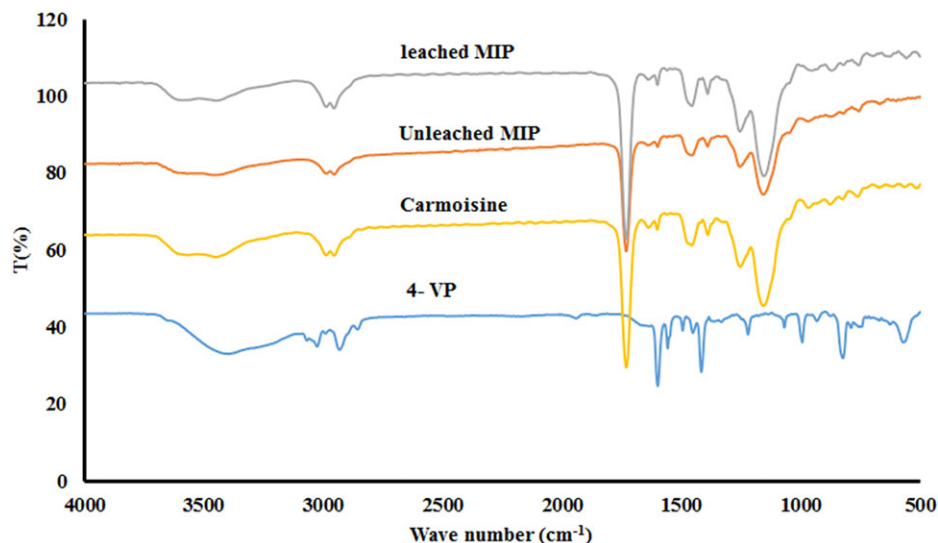

FIGURE 3 FTIR spectra of leached and unleached MIP, 4-VP and carmoisine

10 ppm. The results showed 100% adsorption of the prepared polymer toward carmoisine from juice medium shown in Fig. 2, the same as what was observed in the 10 ppm carmoisine stock solution. It can be demonstrated that there is no matrix interference in the separation of carmoisine from juice medium. Pomegranate juice anthocyanins peak can be also seen at early retention times in the chromatogram shown in Fig. 2. Considering the obtained data, a high potential of synthesized MIP as an adsorbent in SPE cartridges for low concentrations of carmoisine from complicated food matrices can be seen. Furthermore, the synthesized polymer can be applied in biosensors as a selective adsorbent of carmoisine, proving its presence in the matrix.

3.4 | FTIR spectroscopy

FTIR spectroscopy was applied to analyze the molecular structure of the imprinted polymer. The FTIR spectrum of MIP (leached and unleached), functional monomer (4-VP), and the template (carmoisine) are shown in Fig. 3.

Both leached and unleached MIPs had similar IR spectra indicating the similarity in backbone structure. However, template and monomer complexation caused differences in their spectrum. The sharp adsorption peaks at 1500–1700 cm^{-1} were assigned to the C=C and C=N stretching groups of 4-VP and naphthalene ring vibrations of carmoisine. It can be seen that the complex form of MIP had broader peaks. The
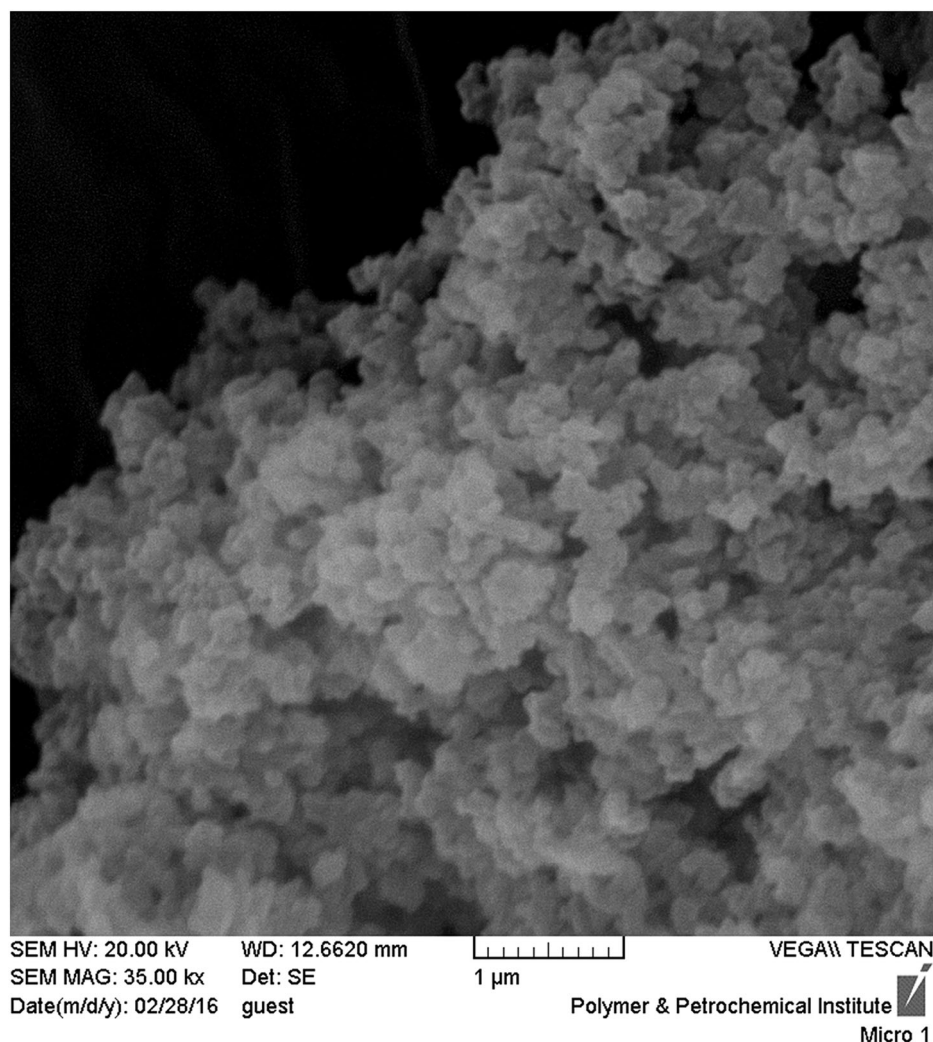
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FIGURE 4 Scanning electron microscopic image of carmoisine-imprinted polymer; carmoisine:4-VP:EGDMA ratio of 1:4:20 in acetonitrile:methanol (80:20)

band at 3300–3500 cm^{-1}, which was broad, corresponded to the stretching vibration of hydrogen bonded –OH and –NH group, while free –OH and –NH group gave a sharp peak in this region as seen in leached MIP spectra. The peak at about 2900 cm^{-1} and also 1100 cm^{-1} corresponded to C–H stretching and vibration in –CH_2 of 4-VP. Azo and sulfonate groups of carmoisine gave bands at 1100–1300 cm^{-1} [1,16]. Considering the peak transformation and sharpness shifting, FTIR results indicated that the template had successfully interacted with functional monomer.

3.5 | Particle size and zeta potential of polymer

The particle size was about 253 and 8.7 nm in length and width, respectively, which was expected in precipitation polymerization. Polydispersity index (PDI) was about 0.5. PDI, which showed the particle size distribution, ranges from 0 to 1 in Zetasizer. For a uniform sample, the PDI would be closer to 0.

Based on zeta potential data, the polymer was negatively (+15.4 mV) charged that indicated poor tendency of polymer particles to aggregation [17]. Slight positive charges of the polymer in aqueous medium can be attributed to basic character and protonated pyridyl groups on 4VP.

3.6 | SEM of imprinted polymer

SEM image of carmoisine imprinted polymer is illustrated in Fig. 4, which was taken at a magnification of 35 000×. The polymer was obtained using 4-VP and EGDMA at a ratio of 4:1 and 20:1 to the template in a diluted medium with acetonitrile/methanol. As can be seen in Fig. 4, the particles had a rough surface.

3.7 | Thermal analysis of polymer

TGA is a thermal analysis that is used to characterize the properties of polymeric materials such as thermal stability and mass loss. Thermal analysis data depend on the molecular
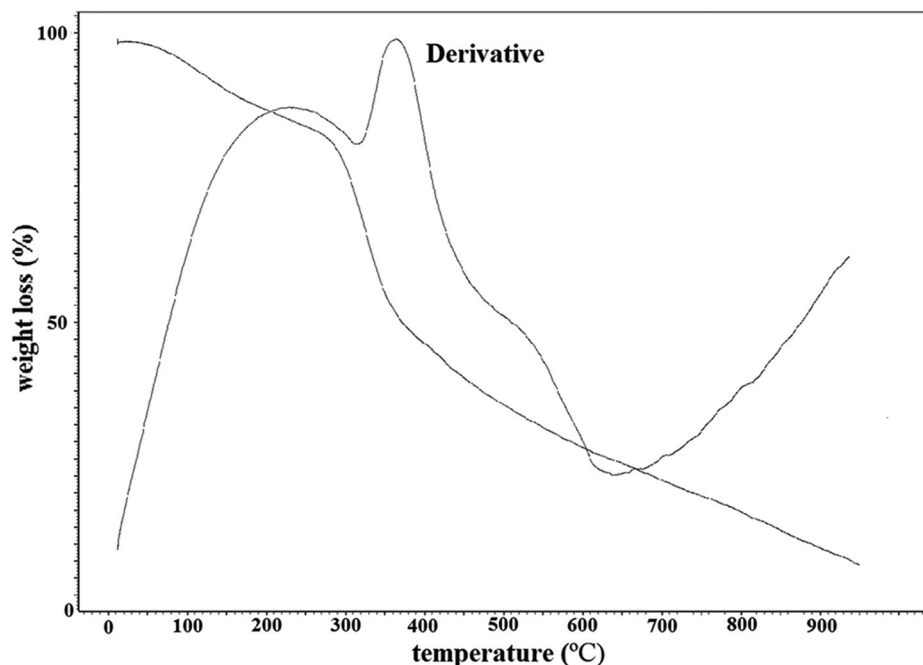
FIGURE 5   Thermal degradation and mass loss of carmoisine-imprinted polymer

weight, polymer architecture, synthesis route, and moisture content [18].

TGA results showed that the carmoisine imprinted polymer underwent thermal degradation beginning at 250°C and with a total mass loss of about 10% that could be attributed to the release of solvent residues. Maximum polymer degradation (sharp degradation step as can be seen in Fig. 5, started at about 300°C and a mass loss of 75% was observed at about 620°C that was attributed to 4-VP-structured polymer. Higher amount of 4-VP improved thermal stability of the polymer [16].

4 | CONCLUDING REMARKS

According to experiments applied in this study for the characterization of carmoisine imprinted polymers, 4-VP polymer as a functional monomer gave the best binding capacity. The critical point of this polymerization method was in the elution stage of template from polymer. The Synthesized MIP had the potential of selective extraction of carmoisine from complex juice medium similar to the carmoisine stock solution. The Prepared MIP can be utilized in sensors or in SPE improving sample preparation by selectivity increment for the detection of carmoisine from pomegranate juice.

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