PCN-222 metal–organic framework: a selective and highly efficient sorbent for the extraction of aspartame from gum, juice, and diet soft drink before its spectrophotometric determination

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Abstract
In this paper, we describe synthesis and application of an iron porphyrinic metal–organic framework PCN-222(Fe) for solid phase extraction of aspartame, an artificial non-saccharine sweetener, from gum, juice and diet soft drink samples prior to its determination by spectrophotometry. The mesoporous MOF was synthesized solvo-thermally and characterized by Fourier transform-infrared spectroscopy, powder X-ray diffraction, scanning electron microscopy, and Brunauer–Emmett–Teller techniques. To obtain the best extraction efficiency of aspartame, significant affecting parameters such as pH of sample solution, amount of the sorbent, type and volume of eluting solvent, and adsorption and desorption times were investigated and optimized. Under optimum conditions, the calibration graph for aspartame was linear in the range of 0.1 to 100.0 mg.L\(^{-1}\) and relative standard deviation of aspartame was 1.7\% (n = 7). Limit of detection of method calculated as 0.019 mg.L\(^{-1}\) and the enrichment factor of 350 folds was obtained. Adsorption capacity of synthesized sorbent was found to be 356 mg.g\(^{-1}\). Hierarchical porosity, the eight terminal–OH groups of the Zr\(_6\) node, and hydrogen bonding possibly play vital role for selective adsorption of aspartame. The optimized method was successfully applied to the determination of aspartame in real samples with reasonable recoveries (> 98%).

Keywords: Aspartame, Zirconium-based metal–organic framework, PCN-222(Fe), Solid-phase extraction, Diet soft drink analysis, Spectrophotometry

Introduction
Aspartame (ASP; N-L-a-aspartyl-L-phenylalanine-1-methyl ester), an artificial sweetener, is mostly used in foods, soft drinks, dietary products and preserved fruits for increase product quality and shelf life [1]. There are some witnesses that support there is a relationship between ASP intake and harmful health issues such as obesity, dental caries, carcinogenicity, neurological problems risk of brain tumour rates, and leukaemia [2, 3]. Therefore, it is necessary to develop a fast, simple and sensitive analytical method for detecting ASP in food stuff. According to the joint Food and Agriculture Organization, World Health Organization, and Expert Committee on Food Additives, acceptable daily intake value of ASP is between 0 and 40 mg/kg body mass per day [4].

Spectroscopy (spectrophotometry, colorimetry and chemiluminescence) [5–7], electrochemical techniques
and chromatography [9] are the most important analytical methodologies which have been developed for the determination of ASP. Among them, high performance liquid chromatography (HPLC) is the most common technique applied for determination of sweeteners, including ASP; but this method suffers from highly toxic organic solvents, long analysis time and high cost.

Spectrophotometry is an attractive common technique with advantages including high precision, high accuracy, and low cost of analysis [10] which is suitable for determination of many organic and inorganic compounds. The main drawbacks associated with this technique are lack of selectivity and unfeasibility of detecting low concentrations of analytes [11]. These problems can be overcome by applying a proper extraction technique prior to performing spectrophotometry.

Solid phase extraction (SPE) is one of the most important sample preparation methods which has been extensively applied for this purpose to separate and pre-concentrate food additives and artificial sweeteners in a wide variety of sample matrices [12]. The advantages of this method include high selectivity, high recovery, good reproducibility, amenability to automation, and low organic solvents requirement [13, 14]. In SPE, sorbent is the most important part which directly affect accuracy, selectivity and sensitivity of the extraction and many researches are focused on the improvement of SPE sorbents [15].

Metal-organic frameworks (MOFs) are a class of crystalline porous materials which are composed of metal ions and organic linkers. They have broad application potentials including adsorption, separation, sensing, drug delivery, detection, catalysis, polymerization, gas storage magnetism, luminescence and removal of toxic materials [16–21] due to their high porosity, large surface areas and tuneable pore size, and in the most cases, the high stability in water [22]. PCN-222(Fe) (PCN stands for porous coordination network) is a mesoporous iron-porphyrinic zirconium-based MOF with molecular formula of Zr6(μ3-O)4(μ3-OH)4(OH)4(H2O)4(FeTPCP)2, FeTPCP = 5,10,15,20-tetrakis (4-carboxyphenyl) porphyrin-iron(III) chloride. The parent-MOF node involves an octahedral Zr6 cluster, capped by four μ3-oxoand fourμ3-OH ligands. Eight of the twelve octahedral edges are linked to FeTPCCPCI (as an heme-like ligand) linkers, while the residual of Zr(IV) coordination sites (after activation process with HCl in DMF) are occupied by eight terminal-OH/H2O ligands (non-bridging groups). The accessible eight terminal-OH/H2O group scan be displaced by carbonate-functionalized molecules via dative bonds [23–26]. This pathway is known as solvent-assisted ligand incorporation method for functionalization of 8-connected Zr6 nodes [23–26]. Moreover, the 3D structure of hierarchically porous PCN-222(Fe) typically affords large accessible surface area and high densities of reactant-accessible. Notably, PCN-222(Fe) MOF exhibited extraordinary thermal, mechanical, and chemical stability (stable solution at pH range of 3–10) [27, 28].

Therefore, we decided to prepare, characterize and apply PCN-222(Fe) MOF as a sorbent for SPE of aspartame, a carboxylic acid-containing functional group molecule, from samples with various matrices. Experimental factors affecting extraction were studied and optimized.

Experimental

Chemicals

All reagents were of analytical grade and utilized without further purification. Zirconium(IV) chloride (ZrCl4), methyl 4-formylbenzoate (C6H4O3), pyrrole (C4H5N), benzoic acid (C6H5O2), Iron(II) chloride tetrahydrate (FeCl2·4H2O), propionic acid (C3H6O2) Chloroform (CHCl3), ethanol (C2H6O), methanol (CH4O), glucose, sucrose, fructose, sodium ascorbate, cyclamate, hydrochloric acid (HCl), N,N’-dimethyl formamide (DMF), sodium hydroxide (NaOH) and tetrahydrofuran (THF) were obtained from Sigma-Aldrich Chemical Company (MO, USA). Reagent grade aspartame was obtained from Merck KGaA (Darmstadt, Germany). Milli-Q® (Merck-Millipore, MA, USA) water (18.3 MΩ cm−1) was used throughout all experiments. A stock standard solution of aspartame (1000 mg L−1) was prepared by dissolving 1.0000 g of it in 1000 mL of distilled water. Working standard solutions were prepared by serial dilutions of the stock solution prior to analysis.

Instrumentation

An Agilent (USA) 1200 series HPLC equipped with an Agilent XDB-C18 column (250 mm × 4.6 mm) and an UV detector at fixed wavelength of 210 nm was used for chromatographic separations. Mobile phase was consisted of a mixture of 50 mL of methanol and 50 mL of 1 L % (v/v) triethylammonium acetate buffer (pH 4.5) at the flow rate of 1.0 mL min−1. Before analysis, all samples were passed through a 0.22 µm nylon filter. Absorption measurements were carried out with a UV–Vis spectrophotometer (UV-2100 RAYLeigh, Beijing, China) by monitoring the absorbance at maximum wavelength of 210 nm. All experiments were performed at least in triplicates and the mean values were used for optimization. A Metrohm (Switzerland) model 630 pH meter was used for pH measurements. Powder X-ray diffraction (PXRD) patterns were recorded on a Philips Xpert diffractometer (Netherlands) with monochromated Cu Kα radiation (λ = 1.5418 Å) at a range of 1° < 2θ < 40°. Fourier transformed infrared (FTIR) spectra were recorded in the range of 4000–5000 cm−1 using KBr pellets on a Perkin Elmer Spectrum-FTIR, version 10.01.00 (USA). The
morphology and chemical composition of the sample was characterized using scanning electron microscopy (SEM, MIRA3 TESCAN, Czech Republic). The specific surface areas in Brunauer–Emmett–Teller (BET) were determined by N\textsubscript{2} adsorption–desorption isotherm at liquid nitrogen temperature (TriStar 3020 II, Micromeritics Instrument Corp., Norcross, GA, USA).

**Synthesis of PCN-222(Fe) MOF**

PCN-222(Fe) MOF was synthesized through five-step synthesis from commercially available based on a previously reported procedure through five-step synthesis [26, 27].

**Solid phase extraction procedure**

A batch SPE method was performed for the extraction of ASP using PCN-222(Fe) MOF as sorbent. 250.0 mL of sample solution was transferred to a beaker and its pH was adjusted to 6.0 using by drop wise addition of either NaOH 0.1 M or HCl 0.1 M solution. 7 mg adsorbent was added to solution and was shaken on a shaker (200 rmp, 10 min) then centrifuged at 4000 rpm for 8 min. The aqueous phase was completely discarded. 700 µL of Ethanol-HCl (99:1 v/v) solution was added to the solid and shook again on a shaker (200 rmp, 15 min). Finally, PCN-222(Fe) MOF was separated from the solution by centrifuging at 4000 rpm for 8 min and the concentration of ASP in elution was determined by UV–Vis spectrophotometry against a blank prepared with the same procedure.

**Results and discussion**

**Characterizations of PCN-222(Fe) MOF**

The powder X-ray diffraction (PXRD) pattern of the prepared PCN-222(Fe) MOF is shown in Fig. 1. It can be observed that the pattern is similar to previous reports [26, 27]. The intensive peaks at $2\theta=2.5, 4.9, 6.6, 7.1$ and $9.9^\circ$ are related to the reflections (1 0 0), (2 0 0), (2 -1 1), (2 0 1), (4 0 0), and (4 -2 1), respectively (CCDC No. 893,545) [22, 27].

Fourier transform infrared (FTIR) spectrum of PCN-222(Fe) MOF is shown in Fig. 2. The peaks at around 1691 and 1417 cm\textsuperscript{-1} are attributed to strong stretching vibration of -COO (asymmetric) and -COO (symmetric) bonds of the carboxylate groups. The peaks at about 1570, 650 and 712 cm\textsuperscript{-1} are due to the out of plane bending of the C-Hs of phenyl rings [29]. After ASP sorption, the intensity peaks at 1700 cm\textsuperscript{-1} and 1570 cm\textsuperscript{-1} decreased and leading to a shift towards lower wave numbers.

The porosity of the prepared MOF was measured by nitrogen adsorption–desorption experiments at 77 K. The typical type IV isotherm and a Brunauer–Emmett–Teller (BET) surface area of 1650 m\textsuperscript{2} g\textsuperscript{-1} were obtained, when the activation procedure was applied (Fig. 3). Density functional theory simulation of the N\textsubscript{2} sorption revealed that the nominal MOF have two types of pores, with sizes of ~1.2 nm and ~3 nm (Fig. 4), respectively, corresponded to triangular micro channels and hexagonal meso channels.

Scanning electron microscope (SEM) image was applied to characterize the morphology of the
as-synthesized PCN-222(Fe), and is shown in Fig. 5. As can be seen in the image of metal–organic framework synthesized, that it has typical rod-like structure which was similar to the reported studies [30].

Optimization of SPE procedure
Several important parameters influencing the extraction efficiency, including pH of the sample solution, amount of adsorbent, type and volume of eluting solvent, and adsorption and desorption time were studied and optimized, as discussed below. A standard solution of 10 mg L\(^{-1}\) of ASP was used for this purpose.

Effect of pH
The pH of the sample solution is one of the most critical parameters in the adsorption of ASP on the MOF which shows its influence by two factors: the form of the analyte and surface binding sites on the adsorbent [31]. pH of a series of ASP standard solutions was varied in the range of 3.0–9.0 and results are shown in Fig. 6. As can be seen, the optimum point occurs at pH 6.0. Mechanism of aspartame adsorption on PCN-222(Fe) MOF can be explained with electrostatic interaction between aspartame and the adsorbent. According to a previous research, zero charge point of PCN-222(Fe) MOF was observed at pH = 6.4 [32]. At pHs other than this value, the surface charge of MOF is charged. On the other hand, isoelectric point of ASP was determined as 5.25 (\(pK_1\) 3.18, \(pK_2\) 7.82) [33]. At pH around 6, MOF is positively charged, while ASP is in anionic form, therefore recovery increases.

Effect of type and volume of the eluent
The effect of eluent type on recovery of ASP from MOF was studied. Methanol, ethanol, acetonitrile, water–HCl (99:1 v/v), methanol-HCl (99:1 v/v) and ethanol-HCl
(99:1 v/v) were tested. Acid concentration should be kept at the lowest possible level to prevent MOF degradation. The obtained results are shown in Fig. 7. A quantitative recovery for the ASP was obtained using ethanol-HCl (99:1 v/v) as eluent, maybe because acid can convert ASP from its anionic form to neutral.

The effect of the volume of eluting solvent was investigated at the range of 200–1000 µL (Fig. 8). The results show that 700 µL of ethanol-HCl (99:1 v/v) is favorable to obtain maximum extraction recovery of ASP. At higher volumes, a diversing effect is observed, probably due to the effect of dilution of eluted ASP.

**Influence of the amount of sorbent**

The effect of dosage of adsorbent on extraction recovery of ASP in the range of 1.0–10.0 mg is shown in Fig. 9. The maximum extraction recovery was obtained when the amount of the MOF was 7.0 mg. As can be seen, only a tiny amount of adsorbent was enough to extract the ASP because of its high adsorption capacity. Thus, 7 mg of the PCN-222(Fe) was utilized for further experiments.

**Effect of adsorption and elution times**

To reach the best equilibrium time, it is necessary to optimize contact time for the analyte adsorption and desorption. Contact times of 2, 5, 10, 15, 20 and 25 min was tested for both extraction and elusion. Results are depicted in Fig. 10. The time required achieving equilibrium for adsorption and elution was 10 min and 15 min, respectively. This fast kinetic is due to high specific surface area and large pores of the synthesized MOF.

**Effect of ionic strength**

The impact of ionic strength on performance of ASP extraction was studied by making the sample solution 0.0–1.0 mol L⁻¹ with respect to sodium chloride, while other experimental conditions were kept constant. The results showed that the absorbance signal of ASP was almost independent of the ionic strength of the solution; hence, all extraction experiments were performed without salt addition.
Effect of sample volume
In order to obtain a high preconcentration factor, the influence of the sample volume on the extraction efficiency of ASP was investigated in the range of 10.0–500.0 mL. The results showed that the recovery of ASP was very efficient (>98%) in a sample volume range of 10–250 mL and after that, recovery decreases. Hence, 250 mL of the sample solution was used in the subsequent studies.

Enrichment factor (EF), defined as the ratio of the sample volume of 250 mL to the final elution volume of 700 µL, was expected to be 357 folds which was closed to the 350 folds experimentally determined.

Effect of interferences
The selectivity of the present method was investigated by analyzing standard solutions containing 10 mg L\(^{-1}\) of ASP in the presence of high amounts of common compounds which are normally co-exist with ASP. The tolerance limit was defined as the maximum concentration of foreign species causing an error of less than ±5% in the determination of ASP. The results which are summarized in Table 1 showed that there are no interferences from the tested species on preconcentration and determination of ASP by suggested method.

Linear range, limit of detection and precision
Under the optimum conditions, the linear range, detection limit, coefficient of determination, enrichment factor, accuracy and precision of the suggested method were obtained and summarized in Table 2. The calibration curve was linear over a concentration range of 0.1–100 mg L\(^{-1}\) with a coefficient of determination (R\(^2\)) of 0.997. Limit of detection (LOD), obtained from

\[3(S_d)_{blank}/m \text{ (where } (S_d)_{blank} \text{ is the standard deviation of ten consecutive measurements of the blank and } m \text{ is the slope of calibration curve), was } 0.019 \text{ mg L}\(^{-1}\). For evaluation of the sorption capacity of MOF, under the optimum conditions of ASP adsorption, 7 mg of this sorbent was added to 250.0 mL of 10 mg L\(^{-1}\) standard solution of ASP and after reaching equilibrium, concentration of remaining ASP was determined using an HPLC by direct injection of 10 µL of the solution and comparison to a calibration curve. Peak areas were used for quantifications.

Adsorption capacity was found to be 356 mg g\(^{-1}\) which was calculated from the following equation [34]:

\[q_e = \frac{(C_0 - C_e) \times V}{m}\]

where C\(_0\) and C\(_e\) are initial and equilibrium concentrations of ASP, V (L) is volume of sample solution and m (g) is the adsorbent dosage. The relative standard deviation (RSD %) of the seven replicate measurements for the same solution was <1.7%. A comparison between the figures of merit of the method applied in this work with other absorbents used for preconcentration and analysis of ASP are summarized in Table 3. As can be seen, and despite expensive and sophisticated instruments used in some methods, still the PCN-222(Fe) MOF sorbent has higher sorption capacity and better LOD due to having large pore size.
Real sample analysis
To assess the performance of this method for the analysis of real samples in complicated matrices, the proposed procedure was applied to the determination of ASP in three different samples, i.e. a soft cola drink, a peach juice and a bubble gum.

Juice was degassed and homogenized for 10 min in an ultrasonic bath and cola drink was degassed by putting on a shaker for 15 min. For bubble gum, one stick (weighing 2.7 g) of it was broken to small pieces (approximately 3 × 3 mm) and transferred to a 120 mL volumetric flask and mixture of acetic acid, water and chloroform (1:50:25 v/v) was added to it and stirred at high speed for 10 min. All final solutions were filtered through 0.45-μm filters and finally 10-mL aliquot of each one was diluted in a 100-mL volumetric flask prior to analysis.

Detectable amount of ASP was observed in all samples (Table 4). To validate trueness of the analyses, a standard HPLC method [35] was also performed. In order to better evaluate the matrix effect, samples were spiked by adding the appropriate amounts of ASP and analyzed according to the MOF-SPE/spectrophotometric method. Average recoveries ranged from 97% to 104%, with RSDs between 1.0 and 3.6% (n = 3) were obtained which clearly show that this procedure can be successfully applied to trace level determination of the ASP sweetener in various samples. As an example, spectrum of a cola sample spiked with 50 μg L⁻¹ of ASP and extracted by MOF-SPE is depicted in Fig. 11.

Conclusion
In this paper, selective batch-mode solid-phase extraction of aspartame was performed by means of a mesoporous porphyrinic metal–organic framework, PCN-222(Fe), followed by its spectrophotometric determination. The MOF showed high adsorption capacity and high extraction efficiency toward this analyte. Method applicability was demonstrated by analysis of three real samples, including soft cola drink, peach juice and bubble gum and results were compared to standard HPLC analysis with satisfactory results. This method has high preconcentration factor (350), good RSD (< 1.7%) and very low

Table 3 Comparison of the proposed method with other methods for the determination of ASP

| Sorbent | Detection technique | LOD (mg L⁻¹) | Sorbent capacity (mg g⁻¹) | linear range (mg L⁻¹) | Enhancement factor | RSD (%) | Ref. |
|---------|---------------------|--------------|---------------------------|-----------------------|-------------------|---------|-----|
| Sephadex G-25 | Spectrophotometry-FIA | 0.3 | NM | 0.001 – 0.2 | NM | 1 | [36] |
| C₁₈ cartridges | HPLC/UV | NM | NM | NM | NM | 3.1 | [37] |
| Monolithic molecularly imprinted polymer | Capillary electrophoresis | NM | NM | 0.0001–0.0004 | NM | 2.7 | [38] |
| Tetraethylenepentamine function-alized Fe₃O₄ magnetic polymer | HPLC | 0.14 | NM | 0.005–0.05 | NM | 3.8 | [39] |
| Ethylenediamine-functionalized magnetic polymer | Ultra-fast liquid chromatography–mass spectrometry | 0.15 | NM | 0.005–0.5 | NM | 1.1–2.8 | [40] |
| PCN-222(Fe) MOF | Spectrophotometry | 0.019 | 356 | 0.0–100 | 357 | 1.7 | This work |

NM Not mentioned

Table 4 Determination of ASP in sweetener samples (n = 3)

| Sample            | ASP content (µg L⁻¹) | Added | Found by HPLC | Found by SPE-MOF | Recovery (%) | RSD (%) |
|-------------------|----------------------|-------|---------------|------------------|--------------|---------|
| Peach juice       | 0                    | 60    | 61            | 101              | 2.2          |
|                   | 50                   | 111   | 112           | 104              | 2.1          |
|                   | 500                  | 550   | 549           | 98               | 1.9          |
| Bubble gum        | 0                    | 20    | 18            | 90               | 3.6          |
|                   | 50                   | 70    | 69            | 98               | 2.5          |
|                   | 500                  | 521   | 519           | 100              | 1.0          |
| Soft cola drink   | 0                    | 100   | 98            | 98               | 1.6          |
|                   | 50                   | 151   | 150           | 100              | 2.5          |
|                   | 500                  | 600   | 598           | 99.6             | 3.6          |
detection limit (19 µg L$^{-1}$). No toxic organic solvents were used during extraction and elution. Spectrophotometric instrumentation owns merits of simplicity, cheapness, portability and so on.

Abbreviations
ASP: Aspartame; HPLC: High performance liquid chromatography; SPE: Solid-phase extraction; MOF: Metal–organic framework; PCN: Porous coordination network; FTIR: Fourier transformed infrared; SEM: Scanning electron microscopy; PXRD: Powder X-ray diffraction; LOD: The limit of detection; Sd: Standard deviation; RSD: Relative standard deviation; BET: Brunauer–Emmett–Teller.

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Authors’ contributions
ZSM performed lab work and wrote the initial draft of manuscript. MKa, MKh and ARO supervised the project, assisting in lab work and revised the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
All data and analyzed or generated during this investigation are included in the manuscript.

Competing interests
The authors declare that they have no competing interests.

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