Synthesis of value-added MIL-53(Cr) from waste polyethylene terephthalate bottles for the high-performance liquid chromatographic determination of methylxanthines in tea

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ABSTRACT

In this work, which was based on the concepts of green chemistry, polyethylene terephthalate (PET) waste bottles were employed as the source of a benzene-1,4-dicarboxylate linker for the synthesis of MIL-53(Cr). Subsequently, the synthesized MIL-53(Cr) was characterized and employed for the first time as a stationary phase for the HPLC determinations of different methylxanthines in black, green, and white tea samples, respectively. As observed, the main working mechanism was the reversed-phase; however, size-exclusion effects were noticeable on catechins, which exceeded the dynamic diameter of MIL-53(Cr) ($\sim$8.5 Å). Under optimal conditions, the MIL-53(Cr) column exhibited the best efficiency for caffeine with 35,300 plates m^{-1} and a chromatographic resolution of $\geq$1.72 for all the detected compounds in the tea samples. The developed method was linear (0.183–200 µg mL^{-1}) and the obtained LOD values were 0.055–0.072 µg mL^{-1}. The obtained RSDs, which were determined employing different chromatographic parameters indicated the feasible reproducibility of the columns and verified the ruggedness of the method. The results confirmed that the methylxanthine contents of the black teas were the highest (51.28–60.02 mg per tea bag; 2.0 g), followed by those of the green teas (26.72–43.68 mg per tea bag), before those of the white teas (20.44–25.36 mg per tea bag). Furthermore, the separation performances of the MIL-53(Cr) column and two silica-based C$_{18}$ commercially columns (3 and 5 µm-sized particles) were compared. The structure of the MIL-53(Cr) afforded higher retention factors in the methylxanthines because of the hydrophobic π–π interactions between the solutes and aromatic ring of the organic linker. Conclusively, the MIL-53(Cr) column, which was prepared from PET bottles, could be applied to the routine analyses of methylxanthines in tea samples.

1. Introduction

Presently, metal–organic frameworks (MOFs) are attracting tremendous attention in the fields of materials and sciences. MOFs are a class of porous crystalline materials that are constructed from metal ions and multidentate organic linkers [1,2]. The fascinating properties of MOF materials coupled with the pore topology of their structures, as well as their diversities and rational tunability, impart them with promising applications [1,3,4] in gas and energy storage [5], sample preparation [6], catalysis [7], sensing [8], biomedicine [9], food industry [10], drug delivery [11], water harvesting [12], adsorption [13], and separation [14]. Owing to their tunability, uniform pore sizes, semi-organic pore walls, large surface areas (SAs), and high thermal stabilities, some classical MOFs, such as MOF-5, ZIF-8, DUT-67(Zr), UiO-66

(Zr), HKUST-1, MIL-47(V), MIL-53(Al/Fe), MIL-100(Fe), MIL-101(Cr), and MIL-125(Ti), have been employed as stationary phases in chromatographic applications [14–20].

Different MOF materials have been synthesized by several approaches. Among them, the hydrothermal/solvothermal process is one of the most conventionally employed ones for preparing MOFs [21]. MOFs are traditionally synthesized by reacting a metal ion with a commercially available organic linker. To function as an effective separation medium, the stationary phase must exhibit excellent stability against pressure and common mobile phase solvents, possess sufficient interaction sites for analyte retention, and possess an adequate pore volume and uniform particle shape and size. However, owing to the abundant options and various synthesis and modification strategies, the selection of appropriate MOF constituents, as well as the control of their reaction conditions, have availed the possibilities of obtaining the desired properties, such as good chromatographic stationary phases.

MIL-n (MIL = Material Institute Lavoisier) is a subclass of MOF materials, which was first synthesized by Gérard Férey's group in 2002 [22]. Different MIL MOFs with linear diamond-shaped networks have been synthesized from trivalent cations (Fe^{3+}, Al^{3+}, Cr^{3+}, Ga^{3+}, V^{3+}, and In^{3+}) and a carboxylic acid ligand. The MIL-53 family is one of the most promising MOFs that can be employed as chemical adsorbents or stationary phases for liquid chromatography (LC) because of their uniform pores, good stability, high surface areas, and significant adsorption affinities [16–18,23–30]. Traditionally, porous MIL-53(Cr) are prepared by mixing Cr^{3+} (a metal center) and benzene-1,4-dicarboxylate (BDC) (a linker molecule) in the presence of hydrofluoric acid and water for three days at 220 °C [31,32]. Recently, green and inexpensive methods were developed in materials and analytical chemistry to minimize costs and mitigate the environmental impacts.

Polyethylene terephthalate (PET) has been widely employed in food-packaging industries since the 1960 s [33]. PET is a lightweight, transparent, chemical which exhibits sufficient resistance and low gas permeability. Typically, PET is employed to produce plastic bottles, which are generally fabricated by the esterification of BDC and ethylene glycol (EG) [34]. Owing to its poor biodegradability, PET is so significant for its role in serious health and environmental issues [35]. However, pure BDC can be obtained by recycling PET waste bottles [35–37]. Since BDC is the main starting material for preparing some MIL MOFs, it is very economical and environmentally valuable to synthesize high value-added materials, such as MOFs, directly by recycling PET wastes. Furthermore, several MOF materials, such as UiO-66(Zr), MIL-47, MIL-53(Cr, Al, or Ga), and MIL-101(Cr), have been synthesized by a similar strategy [35,37,38]. However, there has not been a study on the application of this strategy to adsorption, chromatography, or other analytical chemistry fields. Moreover, this green approach offers an attractive, economic, and environmental approach for preparing value-added materials while eliminating the waste PET stream.

In this work, PET waste bottles were employed as the BDC source to synthesize MIL-53(Cr), thus achieving green chemistry. Although several MIL MOFs have been prepared by regular procedures and utilized as stationary phases in high-performance LC (HPLC) and gas chromatography, the preparation of MIL-53(Cr) by regular procedures and its utilization have not been reported. Furthermore, the produced MIL-53(Cr) was evaluated by scanning electron microscopy (SEM), Fourier-transform infrared (FT–IR), X-ray diffraction (XRD), and specific surface area analyses. This valuable material was subsequently utilized as the stationary phase in the HPLC determination of methylxanthines, including theobromine, theophylline, and caffeine, in black, green, and white tea samples, respectively. The mechanism and separation performance of the MIL-53(Cr)-packed column in HPLC were also investigated under different chromatographic conditions. The analytical merits of the developed method were validated by several parameters. Based on several separation performances and validation parameters, the prepared MIL-53(Cr) column was compared with two silica-based C_{18} commercially packed columns (particle sizes = 3 and 5 μm).

2. Materials and methods

2.1. Chemicals

Chromium (III) chloride hexahydrate (99.9%), hydrofluoric acid (ACS reagent), formic acid (98%–100%), ethanol (99.8%), theobromine (99%), theophylline (99%), and caffeine (98.5%) were purchased from Acros Organics (Morris County, NJ, USA) and Sigma-Aldrich (St. Louis, MO, USA). Exhausted water bottles were employed as PET waste. HPLC-grade acetonitrile was acquired from Fisher Scientific (Leicestershire, UK). Finally, ultrapure water was prepared by an Elix Advantage Milli-Q system (Molsheim, France).

2.2. Samples and the extraction procedures

Three types of commercial teas (black, green, and white teas (Table 1)) were obtained from a local supermarket (Riyadh, Saudi Arabia) as powders in bags and stored at < 0 °C until they were employed. To simulate the common method of preparing tea by consumers, each tea bag (2.0 ± 0.02 g) was placed in 250 mL (a teacup) of boiling distilled water for 2 min. Thereafter, the solution was filtered with a Whatman Grade 44 filter paper on a Buchner funnel to remove the solid particles.

2.3. Synthesis of MIL-53(Cr)

The PET bottle materials, which were cut into small flakes, were utilized as the precursor (instead of terephthalic acid) to synthesize MIL-53(Cr) by a green approach according to Lo et al. [38]. Typically, $CrCl_3 \cdot 6H_2O$ (1.0 mmol), the PET flakes (1.0 mmol), and HF (2.0 mmol) were mixed with 5.0 mL of the ultrapure water in a Teflon-lined stainless-steel autoclave before they were vacuum-heated for 72 h at 210 °C. Thereafter, the autoclave was cooled to room temperature (25.7 °C), and the resulting mixture was filtered. Subsequently, residual PET was removed by solid filtration, and the final product was washed with water and vacuum-dried overnight at 100 °C. This procedure was repeated to obtain the desired quantity of MOFs. The schematic representation of the synthesis procedure and the obtained product (green crystalline MIL-53(Cr) powder) are shown in Fig. 1(A & B).
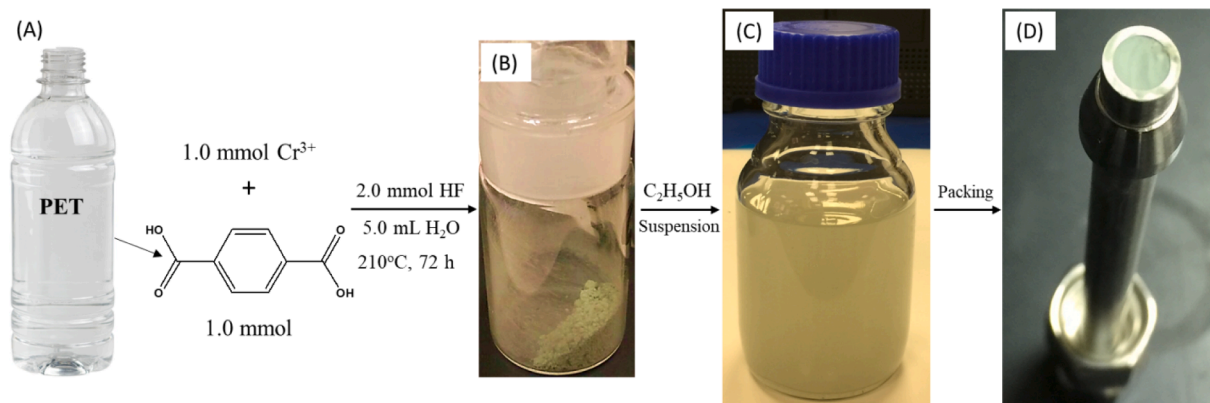
2.4. Preparation of the columns

First, 1.5 g of the synthesized MIL-53(Cr) powder was dispersed in a suitable vessel containing 250 mL of absolute ethanol by sonication for 10 min. Afterward, the suspension (a slurry) was packed into stainless-steel columns (100 and 150 mm (length) × 4.6 mm (i.d.)) and subjected to a pressure of 7000 psi (482.6 bar) for 30 min employing a Restek dual-piston packing pump (Bellefonte, PA, USA). Stainless-steel

Table 1
Tea samples and the average content of theobromine, theophylline, and caffeine (mg per tea bag ± %RSD) (n = 3) in commercial tea samples.

Tea sample	Content in mg per tea bag ± %RSD (n = 3)		
	theobromine	theophylline	caffeine
black teas			
1	0.96 ± 6.34	ND	60.02 ± 4.21
2	0.87 ± 4.19	traces	57.28 ± 5.55
3	0.92 ± 5.68	ND	51.28 ± 5.26
green teas			
4	0.88 ± 7.53	traces	35.48 ± 10.40
5	0.54 ± 7.04	ND	43.68 ± 6.77
6	0.76 ± 5.48	ND	26.72 ± 6.03
white teas			
7	0.58 ± 7.45	traces	20.44 ± 8.60
8	0.49 ± 5.97	ND	25.36 ± 6.73

ND: not detected, traces: the concentration located between LOD and LOQ.

Fig. 1. (A) Schematic illustration of the synthesis procedure of MIL-53(Cr), (B) The obtained MIL-53(Cr) powder, (C) The suspension of MOF powders in ethanol, and (D) Photograph of the prepared column.

frits with pore sizes of 0.5 μm were employed to place the stationary phase inside the column. The prepared columns were conditioned by HPLC-grade acetonitrile for 3 h at a flow rate of 0.10 mL min^{-1} before the analysis.

2.5. Instrumentation and characterization of the columns

The analyses were performed on a Shimadzu HPLC system consisting of an LC-20AD liquid chromatograph, an SPD-M20A diode-array detector, a SIL-20A autosampler, a DGU-20A5R degasser, and a CTO-20A column oven (Kyoto, Japan). The Shimadzu LCsolution software was employed to control the system and acquire the results.

The SEM investigation of the synthesized MOF was performed on a Jeol JSM-6610LA microscope at 20 kV (Tokyo, Japan). The FT–IR spectrum of the prepared MIL-53(Cr) was recorded on a Thermo Nicolet 6700 spectrophotometer (Madison, WI, USA). The MOF powder was mixed with KBr, and the spectra were measured in the range of 4000–400 cm^{-1}. Further, the XRD patterns were obtained at room temperature (25.7 °C) by a Bruker D2 PHASER with that was equipped an XFlash detector (Madison, WI, USA) employing Cu-Kα radiation (λ = 0.15418 nm) in the 2θ range of 5°–40°. The nitrogen adsorption–desorption isotherms, which were measured on a Gemini VII 2390 Micromeritics Surface-Area Analyzer (Norcross, GA, USA), were employed to estimate the surface area and pore sizes of the prepared MOFs at −196 °C. Furthermore, the synthesized MOFs were ground and degassed at 200 °C before the measurements.

2.6. Chromatographic parameters and validation

The developed method was validated by the following parameters: its limit of linearity (LOL), the limit of detection (LOD), and limit of quantification (LOQ), as well as its precision, strength, and recovery. The LOD and LOQ values were measured regarding the concentrations of the analytes that yielded S/N of 3 and 10, respectively. The peak areas were plotted against the various concentrations of the analytes to study the linearity of the method. The LOL values were assessed by the linear regression analysis of the peak areas versus the concentrations of the analytes employing the least square method. Additionally, calibration curves were directly constructed for the analytes before the tea samples were analyzed. The solutions and real samples were filtered by a 0.45-μm filter before they were injected (each solution was injected in three replicates).

For the comparative study, two Betasil C$_{18}$ columns (length, 15 cm and inner diameter, 4.6 mm packed with 3 and 5 μm-sized particles) were purchased from Thermo Scientific (Waltham, MA, USA), and their efficiencies were investigated and compared. Furthermore, various chromatographic parameters, including the retention time (t_R), width at

half peak ($w_{0.5}$), number of theoretical plates (N), retention factor (k), chromatographic resolution (R_s), and asymmetry factor (A_s), were also investigated. The void times (t_0s) of the columns were measured by injecting acetonitrile and recording the signal of the repeatable perturbation. The injection volume was fixed at 5 μL in all the cases.

3. Results and discussion

3.1. Characterization of the synthesized MIL-53(Cr)

MIL-53(Cr) was prepared by a green synthesis approach. The reaction mixture consisted of 2.0 mmol HF, which was added to accelerate the depolymerization of PET. The depolymerization of PET into BDC and EG mostly occurred at the C–O link of the ester in PET since it is the weakest bond therein [39]. After cooling the autoclave to room temperature, residual PET was separated by handpicking and solid filtration since its pieces were larger than the MIL-53(Cr) powders. The green crystalline MIL-53(Cr) product was obtained, as shown in Fig. 1(B). Regarding the weight of residual PET, the yield of this hydrothermal reaction did not exceed 53%. However, the procedure was repeated to obtain the desired quantity of MIL-53(Cr).

Further, the synthesized MIL-53(Cr) was investigated by SEM (Fig. S1(A)), FT–IR (Fig. S1(B)), XRD (Fig. S1(C)) (Supporting Material), and surface area analyses. As shown in Fig. S1(A), the SEM image revealed that MIL-53(Cr) possessed irregular shapes with a particle-size distribution of 0.92–2.46 μm. The FT–IR spectrum (Fig. S1(B)) of the synthesized MOF was obtained at 25.7 °C in the region of 4000–400 cm^{-1}. The peaks at 1400–1700 cm^{-1} correspond to the coordination between O–C=O and Cr^{3+}. The bands at 1421, 1440, and 1526 cm^{-1} were attributed to the symmetric and asymmetric stretchings of the carboxylate groups. The vibrations at 462 and 596 cm^{-1} revealed the Cr–O band in MIL-53(Cr). Further, regarding the XRD spectrum (Fig. S1 (C)), the distinctive signals at 2θ = 8.7°, 10.2°, 12.7°, 15.1°, 18.3°, 19.2°, and 26.8° revealed the successful synthesis of the MIL-53(Cr) crystal structure. Conversely, the sharp peaks between 5° and 30° correspond to the formation of highly crystallized MOF structures. The specific surface area (1057 m^2 g^{-1}) and the pore size (~8.5 Å) of the synthesized MIL-53(Cr) were obtained by the Brunauer–Emmett–Teller (BET) technique. This large surface area contributed to the performance of the stationary phase materials. The SEM, FT–IR, XRD, and surface area characteristics are in good agreement with the results that were obtained for MIL-53(Cr), which were prepared by the regular procedure [21,31,39,40].

3.2. Evaluation of the columns

The typical quantities of MIL-53(Cr) that were required to pack the

columns were 0.757 ± 0.008 g for the 150-mm-long columns and 0.510 ± 0.010 g for the 100-mm-long ones. Furthermore, the prepared MIL-53 (Cr) packed columns were conditioned by acetonitrile for 3 h at a flow rate of 0.10 mL min^{-1} before the analysis. Fig. 1(C & D) show the photographs of the MIL-53(Cr) powder suspensions and one of the prepared columns, respectively.

The stabilities of the prepared columns were examined. Water and acetonitrile were eluted from the columns to measure the backpressure at different flow rates in the range of 0.05–0.50 mL min^{-1}. The relationship between the flow rate of the solvents and the column backpressure is shown in Fig. S2(A). The column backpressures increased linearly over the flow rate ranges of the mobile phase at a constant temperature. The linear dependence with correlation coefficients (R^2), which were ≥0.9981, demonstrated the good permeability and mechanical stability of the prepared MIL-53(Cr) packed columns. Although the columns exhibited increased backpressures of water based on the viscosity of the solvent, the pressure drops in the columns did not exceed 3300 psi (227.5 bar) in all the cases, and this was beneficial to prolonging the lifetime of the chromatographic columns. As shown in Fig. S2(B), the MIL-53(Cr) packed column exhibited excellent stability during the pressure drops (±7 psi) as the water was passed through it for more than seven successive days at 0.25 mL min^{-1}. The stability of the stationary phase was also investigated against the temperature of the column. Fig. S2(C) reveals that the column backpressures decreased

linearly at 30 °C–70 °C when water and acetonitrile were utilized as the eluents at a fixed flow rate (0.25 mL min^{-1}). The decrease in the backpressure of the column corresponds to 36 ± 3 and 32 ± 4 psi for water and acetonitrile, respectively, at every 5 °C increase in the temperature of the column. Ultimately, the MIL-53(Cr) stationary phase and prepared columns did not reveal significant defects in their stability under the applied chromatographic conditions.

Subsequently, the MIL-53(Cr) packed columns were employed to separate a mixture of three methylxanthines (theobromine, theophylline, and caffeine). Two-column dimensions were prepared (lengths of 100 and 150 mm with the same i.d. (4.6 mm)). However, the shorter column (100 mm) did not demonstrate adequate efficiency for the separations of the theobromine and theophylline isomers under the examined conditions. For example, Fig. 2(A) shows the typical separation chromatogram of the methylxanthines utilizing the 100 mm-long MIL-53(Cr) column with water/acetonitrile (50:50, v/v) at 0.30 mL min^{-1}. Thus, MIL-53(Cr), which was prepared inside the 150 mm-long stainless-steel column, was employed for the subsequent experiments.

The methylxanthines mixture was injected to examine the separation performance of the 150 mm-long MIL-53(Cr) column under different conditions. Fig. 2(B) shows the typical separation of the methylxanthines in ~ 8.4 min at 0.35 mL min^{-1} utilizing water/acetonitrile (40:60, v/v) as the isocratic mobile phase at a detection wavelength of 273 nm. Under the optimized conditions, the MIL-53(Cr) column
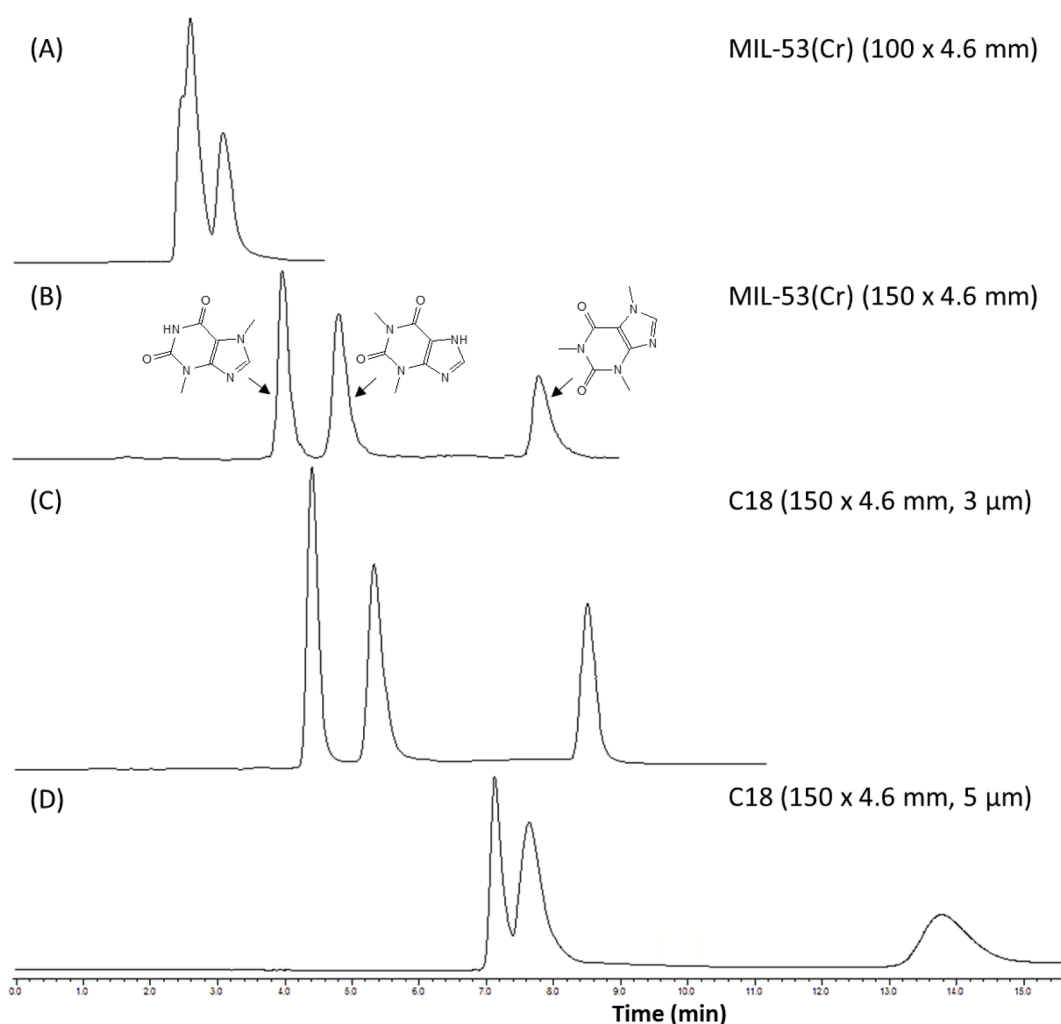

Fig. 2. Chemical structures and chromatograms of the 1.0 µg mL^{-1} theobromine, theophylline, and caffeine mixed standard solution on MIL-53(Cr) 100 mm long column using water/acetonitrile (50:50, v/v) at 0.30 mL min^{-1} flow rate (A), MIL-53(Cr) 150 mm long column using water/acetonitrile (40:60, v/v) at 0.35 mL min^{-1} flow rate (B), C$_{18}$, 3 µm particle size column using water/acetonitrile (30:70, v/v) at 0.35 mL min^{-1} flow rate (C), C$_{18}$, 5 µm particle size column using water/acetonitrile (55:45, v/v) at 0.30 mL min^{-1} flow rate (D).

exhibited the best efficiency for caffeine at 35,300 plates m^{-1} with R_s of ˃2.74. Moreover, negligible peak tailings, which were determined at 10% of the peak heights of the three methylxanthines, were obtained with suitable A_s (1.18, 1.16, and 1.33). t_R, the efficiency regarding the theoretical plates, k, R_s, and A_s of the separations of the methylxanthines were measured under optimum conditions and reported in Table 2.

3.3. Optimization and merits of the developed HPLC method

A series of experiments was accomplished to validate the suitability of this analytical approach for analyzing real samples. The calibration curves of theobromine, theophylline, and caffeine were established by injecting standard solutions that were prepared in water (Fig. S3(A)). At the peak areas under signal evaluation, the developed method was linear in the ranges of 0.183–170, 0.227–170, and 0.240–200 µg mL^{-1} for theobromine, theophylline, and caffeine, respectively. Thus, good linearity with R^2 of ≥0.9993 was achieved in this concentration range for the three compounds. The typical calibration curves of the three analytes are presented in Table 3. The LOD values of the assay (0.055, 0.068, and 0.072 µg mL^{-1} for theobromine, theophylline, and caffeine, respectively) were determined according to the signal-to-noise criteria (S/N) of 3. The experimental results of LOD, LOQ, and LOL are presented in Table 3.

For the precision test, the methylxanthines were repeatedly injected for three successive weeks, as shown in Fig. S4. RSDs of t_R and the peak areas for the injection to injection, day to day, and week to week reproducibilities on the same column were ≤1.83% and ≤4.16%, respectively. The obtained RSDs values revealed the reasonable reproducibility of the prepared packed columns. Further, the toughness of the developed method against small changes in the flow rate and composition, column temperature, and detection wavelength of the mobile phase was determined by calculating the t_R, N, and R_s values, and the experimental results are presented in Table S1. The obtained results were compared with those that were obtained under the optimal conditions, and the values verified the toughness of the developed method.

3.4. Analyses of real samples

The reliabilities and applicabilities of the prepared MIL-53(Cr) columns and optimized method for analyzing real samples were studied by injecting various tea water extracts. The method proved to be effective, sensitive, and reproducible for the determination of methylxanthines in the three types of teas (black, green, and white) and eight commercial tea samples. Fig. 3(A, B, & C) show the successful separation chromatograms of some contents of the three tea water extracts. Under the optimum conditions, a complete baseline separation was accomplished for the constituents of all the tea samples at high R_s (≥1.72). The elution

Table 2

Peak parameters for the separation of the xanthines using MIL-53(Cr) (150 mm long × 4.6 mm i.d.), C$_{18}$ (150 mm long × 4.6 mm i.d., 3 µm particle size), and C$_{18}$ (150 mm long × 4.6 mm i.d., 5 µm particle size) columns under the optimized conditions.

Analyte	t_R	N	k	R_s	A_s	column
theobromine	3.96	20,900	1.29	–	1.18	MIL-53(Cr) (150 × 4.6 mm)
theophylline	4.82	20,800	1.79	2.74[a]	1.16	
caffeine	7.83	35,300	3.53	7.78[b]	1.32	
theobromine	4.41	25,900	1.23	–	1.11	C$_{18}$ (150 × 4.6 mm, 3 µm)
theophylline	5.32	22,300	1.69	2.80[a]	1.09	
caffeine	8.49	42,600	3.28	8.02[b]	1.25	
theobromine	7.12	45,300	0.87	–	1.13	C$_{18}$ (150 × 4.6 mm, 5 µm)
theophylline	7.63	19,400	1.01	1.12[a]	1.37	
caffeine	13.77	16,400	2.62	7.34[b]	1.29	

t_R: retention time (min), N: number of theoretical plates (plates m^{-1}), k: retention factor, R_s: chromatographic resolution, A_s: asymmetry factor at 10% of peak height, [a]resolution between theobromine and theophylline, and [b]resolution between theophylline and caffeine.

Table 3

Analytical parameters of the developed method using MIL-53(Cr) (150 mm long × 4.6 mm i.d.), C$_{18}$ (150 mm long × 4.6 mm i.d., 3 µm particle size), and C$_{18}$ (150 mm long × 4.6 mm i.d., 5 µm particle size) columns.

analyte	regression equation	R^2	LOD	LOQ	LOL	column
theobromine	A = 88836c + 5009	0.9997	0.055	0.183	170	MIL-53(Cr) (150 × 4.6 mm)
theophylline	A = 88084c + 3048	0.9994	0.068	0.227	170	
caffeine	A = 72049c + 7393	0.9993	0.072	0.240	200	
theobromine	A = 111883c + 16669	0.9998	0.039	0.130	120	C$_{18}$ (150 × 4.6 mm, 3 µm)
theophylline	A = 106204c + 13313	0.9994	0.046	0.153	120	
caffeine	A = 95109c + 7498	0.9996	0.054	0.180	150	
theobromine	A = 52256c + 2947	0.9995	0.082	0.273	180	C$_{18}$ (150 × 4.6 mm, 5 µm)
theophylline	A = 53384c + 1844	0.9995	0.080	0.267	180	
caffeine	A = 42886c + 5401	0.9988	0.126	0.420	200	

LOD, LOQ, and LOL: limit of detection, quantification, and linearity, respectively (µg mL^{-1}), A: peak area, and c: analyte concentration.

order (gallic acid, theobromine, theophylline, and caffeine) agreed with their hydrophobicities, as demonstrated in the reversed-phase mode. By comparison, in the separation of the tea water extracts by a commercial C$_{18}$ column (150 × 4.6 mm, 3 µm), two catechin compounds ((+)-catechin and (−)-epigallocatechin) were eluted before the gallic acid and three methylxanthines regardless of the mobile phase composition owing to the size-exclusion effect (Fig. 3(D)). Since they could not access the pores of the MIL-53(Cr) structure with a dynamic diameter of ∼8.5 Å, the large compounds exhibited lowered retentions owing to the size-exclusion effect. Regarding the sequence of the identified compounds, the main working mode of the MIL-53(Cr) stationary phase was the reversed-phase mechanism and the size-exclusion effect for the large molecules.

Table 1 summarizes the average theobromine, theophylline, and caffeine contents of the studied commercial teas. The results confirmed that the methylxanthine contents of the black tea samples were the highest, followed by those of the green and white tea samples, successively. The average caffeine contents of the black, green, and white teas per tea bag (2.0 g) were 51.28–60.02, 26.72–43.68, and 20.44–25.36 mg, respectively. However, theophylline was only detected in trace amounts or not detected at all in some of the tea samples. The extraction procedure was repeated three times for each tea type, and the %RSD values were <10.4 in all the cases. The average caffeine contents correlated reasonably with those that were reported in the literature [41–43]. Conversely, since the tea water extract generally consisted of other organic compounds, such as polyphenols [44,45], the later eluted contents of the sample matrix were washed from the column with acetonitrile after each run.

The recovery experiment was performed to evaluate the applicability of the proposed method to the determination of methylxanthines, and the tea sample (Sample 4) was selected as the model for this study. The experiments were performed by spiking the real sample extracts with methylxanthines at three (low, medium, and high corresponding to 1.0, 10, and 50 µg mL^{-1}, respectively) concentration levels. The measured recovery ranged between 87.02% and 96.03% with an RSD value of ≤3.77% (n = 3) in all the cases. These values demonstrated the good efficiency of the extraction procedure. The spike recovery percentages and %RSD values of Sample 4 are presented in Table S2. From these experiments, it was concluded that the MIL-53(Cr) column, which was prepared from PET bottles, could be applied to the routine analyses of methylxanthines in tea samples.
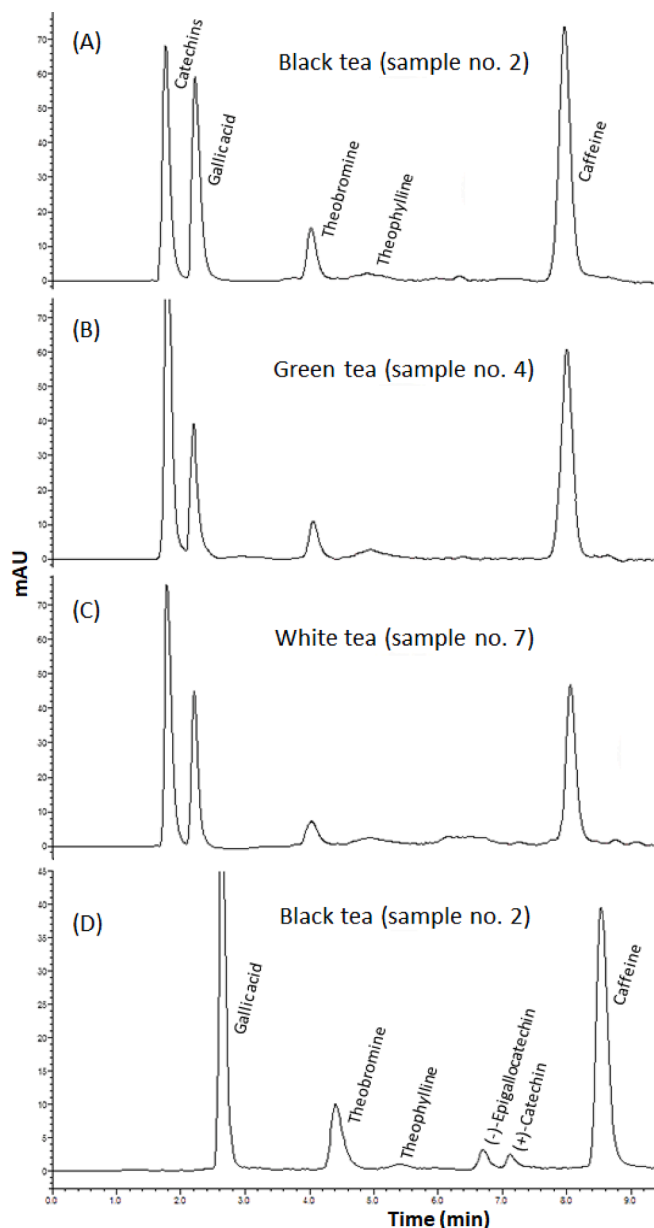
Fig. 3. Representative HPLC chromatograms for some of the studied samples. (A) sample no. 2, (B) sample no. 4, and (C) sample no. 7. Separation conditions are as shown in Fig. 2(B). (D) sample no. 2. Separation conditions are as shown in Fig. 2(C).

3.5. Comparative study

The performance of the prepared MIL-53(Cr) column was compared with those of many widely employed conventional particulate packed C_{18} columns. Therefore, two columns, which were packed with 3- and 5-μm particulate octadecyl–silica with the same dimensions as those of the prepared MIL-53(Cr) column (150 mm (length) × 4.6 mm (i.d.)), were employed. The two columns were run under the optimum conditions for separating methylxanthines, and the results were compared with those of the prepared MIL-53(Cr) column regarding some chromatographic and method-validating parameters. The typical chromatograms for the separations of methylxanthines by the 3- and 5-μm particle-size C_{18} columns are shown in Fig. 2(C & D), respectively. To demonstrate the compromise between R_s and the runtime for separating the methylxanthines, each column was run at its optimum level employing the same mobile phase solvents and different isocratic conditions.

As shown in Fig. 2(C), the complete separation of the methylxanthines was accomplished with the conventional C_{18} column containing the 3-μm particles in ~ 9 min at a water/acetonitrile (30:70, v/v) mobile phase flow rate of 0.35 mL min^{-1}. Conversely, Fig. 2(D) shows that the separation time extended to 15 min with the C_{18} column containing the 5 μm-particles at a lower flow rate (0.30 mL min^{-1}) and with a higher water mobile phase content (55%). Under the optimum conditions, the prepared MIL-53(Cr) packed column separated the three methylxanthines at comparable resolutions with those of C_{18} (the 3 μm commercial columns) in a slightly shorter runtime. The structure of the MIL-53(Cr) stationary phase increased k of the three methylxanthines, as presented in Table 2. The highest k was 3.53 for caffeine employing the MIL-53(Cr) column compared to 3.28 and 2.62 obtained with the C_{18} (3 and 5 μm) columns. This could be due to the hydrophobic π–π interactions between the solutes and the aromatic ring of the organic linker of the MIL-53(Cr) framework. Contrarily, the k values of the three analytes, which were between 1.29 and 3.53, revealed a good compromise between R_s and the runtime.

The separation efficiencies of the prepared MIL-53(Cr) column and the commercial C_{18} ones were compared. Although the flow rate of the mobile phase fluctuated from 0.10 to 0.50 mL min^{-1}, the efficiency of the column was evaluated regarding Ns and their height equivalents for each compound. Fig. S3(B) shows the van Deemter curves of caffeine that were calculated for the three columns. The prepared MIL-53(Cr) column demonstrated the best efficiency for caffeine (35,300 plates m^{-1} at 0.35 mL min^{-1}). Conversely, the measured N values of caffeine were 42,600 and 16,400 plates m^{-1} for the 3- and 5-μm particle packed C_{18} columns, respectively, at the optimum flow rates. Moreover, the registered peak-tailing values of the compounds were low and almost the same. The A_s values, which were determined at 10% of the peak heights of the three columns, were between 1.09 and 1.37 in all the cases. The comparison results of the chromatographic parameters for the performance of the columns are presented in Table 2.

The validation parameters of the analytical methods were also compared between the columns. Fig. S3(A) shows the calibration curves of caffeine in MIL-53(Cr) and the two commercial C_{18} columns. Based on the LOD and LOQ values, the prepared MIL-53(Cr) column displayed better analytical sensitivity compared with the commercial C_{18} (5 μm) one. However, among the three columns, C_{18} (3 μm) exhibited the lowest LOD and LOQ values. Conversely, the MIL-53(Cr) packed column exhibited higher LOLs (comparable with those of C_{18} (5 μm) than the C_{18} (3 μm) one for all the compounds. The obtained results were due to the porous structure of the MIL-53(Cr) stationary phase, which improved the loading capacity and increased the dilution of the analytes inside the column. Moreover, the porous structure of MIL contributed to the reduction of the backpressure of the column compared with the case of the particulate packed columns, and this benefited the lifetime of the column. The parameters for assessing the analytical performance of the developed method for the three columns are listed in Table 3.

The prepared MIL-53(Cr) packed column was compared with the commercial C_{18} ones (synthesized by the sol–gel condensation of alkoxysilanes), which are the most utilized columns for analyzing methylxanthines and tea samples, by the Analytical Eco-Scale method from the green chemistry viewpoint [46]. The proposed approach for preparing MOFs, i.e., from PET bottles, conformed more to the principles of green chemistry compared with that for preparing the commercially available C_{18} modified silica-based packing materials. The penalty points in each case were estimated and summarized in Table S3. The data proved that prepared MIL-53(Cr) was an attractive alternative to the commercial C_{18} packed columns for the routine determinations of methylxanthines in tea.

4. Conclusions

This work in which waste PET bottles were utilized as the BDC linker source to synthesize value-added MIL-53(Cr) MOFs, which were

employed as the stationary phase for the HPLC determinations of methylxanthines in black, green, and white tea samples, applied the concepts of green chemistry. Based on the elution order of the methylxanthines and effects of the mobile phase composition, the main working mode was the reversed-phase mechanism, as well as the size-exclusion effects on the large compounds, which exceeded the dynamic diameter of MIL-53(Cr) (~8.5 Å). The prepared columns exhibited good stability and long-term durability under the following chromatographic conditions: mobile phase solvents: water/acetonitrile, flow rate: 0.05–0.50 mL min^{-1}, column backpressure: ~230 bar, and temperature: 25 °C–70 °C. Compared with the most commonly utilized commercial HPLC columns (silica-based C$_{18}$ columns), the prepared MIL-53(Cr) packed column completely separated the three methylxanthines at a resolution that was comparable with that of the C$_{18}$ (3 μm) commercial column although with a slightly lower runtime. The structure of MIL-53(Cr) afforded higher k values owing to the hydrophobic π–π interactions between the solutes and the aromatic ring of the organic linker in the MIL-53(Cr) framework. The chromatographic performance of MOFs can still be improved, and further studies are required to enhance the efficiency and applicability of these promising materials. The interesting properties of MOFs, as well as their tremendous diversities and tunability of their end structures, will undoubtedly avail many ideas and application options. Moreover, the prepared MIL-53(Cr) column and validated method could be applied to the routine analyses of methylxanthines in tea samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2021.106294.

References

[1] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, Science 341 (2013) 1230444.
[2] S.R. Batten, N.R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M.P. Suh, Reedijk, J. Pure Appl. Chem. 85 (2013) 1715–1724.
[3] T. Qiu, Z. Liang, W. Guo, H. Tabassum, S. Gao, R. Zou, ACS Energy Lett. 5 (2020) 520–532.
[4] K.M.L. Taylor-Pashow, J. Della Rocca, Z.G. Xie, S. Tran, W.B. Lin, J. Am. Chem. Soc. 131 (2009) 14261–14263.
[5] L.J. Murray, M. Dinca, J.R. Long, Chem. Soc. Rev. 38 (2009) 1294–1314.
[6] N. Manousi, G.A. Zachariadis, E.A. Deliyanni, V.F. Samanidou, Molecules 23 (2018) 2896–2917.
[7] M.S. El-Shall, V. Abdelsayed, A.E.R.S. Khder, H.M.A. Hassan, H.M. El-Kaderi, T.E. J. Reich, Mater. Chem. 19 (2009) 7625–7631.
[8] L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, Chem. Rev. 112 (2012) 1105–1125.
[9] J. Yang, Y.-W. Yang, Small 16 (2020) 1906846.
[10] P.-L. Wang, L.-H. Xie, E.A. Joseph, J.-R. Li, X.-O. Su, H.-C. Zhou, Chem. Rev. 119 (2019) 10638–10690.
[11] P. Horcajada, C. Serre, M. Vallet-Regi, M. Sebban, F. Taulelle, G. Férey, Angew. Chem. Int. Ed. 45 (2006) 5974–5978.
[12] H. Kim, S. Yang, S.R. Rao, S. Narayanan, E.A. Kapustin, H. Furukawa, A.S. Umans, O.M. Yaghi, E.N. Wang, Science 356 (2017) 430–434.
[13] T. Saeed, A. Naeem, I. Ud Din, M.A. Alotaibi, A.I. Alharthi, I.W. Khan, N.H. Khan, T. Malik, Microchem. J. 159 (2020), 105579.
[14] J.-R. Li, J. Sculley, H.-C. Zhou, Chem. Rev. 112 (2012) 869–932.
[15] Y. Yu, Y. Ren, W. Shen, H. Deng, Z. Gao, TrAC 50 (2013) 33–41.
[16] J. Zhang, Z.J. Chen, Chromatogr. A 1530 (2017) 1–18.
[17] X. Zhao, Y. Wang, D.-S. Li, X. Bu, P. Feng, Adv. Mater. 30 (2018) 1705189.
[18] K. Yusuf, A. Aqel, Z.J. ALOthman, Chromatogr. A 1348 (2014) 1–16.
[19] Z.-Y. Gu, C.-X. Yang, N. Chang, X.-P. Yan, Acc. Chem. Res. 45 (2012) 734–745.
[20] X. Wang, N. Ye, Electrophoresis 38 (2017) 3059–3078.
[21] R.I. Walton, Chem. Soc. Rev. 31 (2002) 230–238.
[22] F. Millange, C. Serre, G. Férey, Chem. Commun. (2002) 822–823.
[23] H.-Y. Huang, C.-L. Lin, C.-Y. Wu, Y.-J. Cheng, C.-H. Lin, Anal. Chim. Acta 779 (2013) 96–103.
[24] Q. Wei, C. Lian, H. Su, D. Gao, S. Wang, Micropor. Mesopor. Mat. 288 (2019) 109574–109579.
[25] Z. Yan, W. Zhang, J. Gao, Y. Lin, J. Li, Z. Lin, L. Zhang, RSC Adv. 5 (2015) 40094–40102.
[26] S.-S. Liu, C.-X. Yang, S.-W. Wang, X.-P. Yan, Analyst 137 (2012) 816–818.
[27] L. Alaerts, M. Maes, L. Giebeler, P.A. Jacobs, J.A. Martens, J.F.M. Denayer, C.E. A. Kirschhock, D.E. De Vos, J. Am. Chem. Soc. 130 (2008) 14170–14178.
[28] L. Shu, S. Chen, W.-W. Zhao, Y. Bai, X.-C. Ma, X.-X. Li, J.-R. Li, P.J. Somsundaran, Sep. Sci. 39 (2016) 3163–3170.
[29] M. Maes, F. Vermoortele, L. Alaerts, S. Couck, C.E.A. Kirschhock, J.F.M. Denayer, D.E. De Vos, J. Am. Chem. Soc. 132 (2010) 15277–15285.
[30] R. El Osta, A. Carlin-Sinclair, N. Guillou, R.I. Walton, F. Vermoortele, M. Maes, D. De Vos, F. Millange, Chem. Mater. 24 (2012) 2781–2791.
[31] C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer, G. Ferey, J. Am. Chem. Soc. 124 (2002) 13519–13526.
[32] K.-S. Lin, A.K. Adhikari, M.-T. Tu, C.-H. Wang, C.-L. Chiang, J. Nanosci. Nanotechnol. 13 (2013) 2549–2556.
[33] S.B. Wang, C.S. Wang, H.P. Wang, X.L. Chen, S.B. Wang, Polym. Degrad. Stab. 114 (2015) 105–114.
[34] F. Awaja, S. Pavel, Eur. Polym. J. 41 (2005) 1453–1477.
[35] X. Dyosiba, J. Ren, N.M. Musyoka, H.W. Langmi, M. Mathe, M.S. Onyango, SM&T 10 (2016) 10–13.
[36] S. Cavalcante, D. Vieira, I. Melo, Proceedings 41 (2019) 78–86.
[37] J. Ren, X. Dyosiba, N.M. Musyoka, H.W. Langmi, B.C. North, M. Mathe, M. S. Onyango, Int. J. Hydrog. Energy 41 (2016) 18141–18146.
[38] S.-H. Lo, D.S. Raja, C.-W. Chen, Y.-H. Kang, J.-J. Chen, C.-H. Lin, Dalton Trans. 45 (2016) 9565–9573.
[39] R.J. Ehrig, Plastics Recycling: Products And Processes, Hanser Publishers, New York, USA, 1992, p. 1992.
[40] X. Li, J. Zhang, W. Shen, S. Xu, Mater. Lett. 255 (2019), 126519.
[41] A. Aqel, A. Almulla, A. Al-Rifai, S.M. Wabaidur, Z.A. ALOthman, A.-Y. Badjah-Hadj-Ahmed, Int. J. Anal. Chem. 2019 (2019) 2926580.
[42] L.-S. Lee, S.-H. Kim, Y.-B. Kim, Y.-C. Kim, Molecules 19 (2014) 9173–9186.
[43] V. Sharma, A. Gulati, S.D. Ravindranath, V. Kumar, J. Food Compos. Anal. 18 (2005) 583–594.
[44] W. Koch, J. Zagórska, Z. Marzec, W. Kukula-Koch, Molecules 24 (2019) 4277–4305.
[45] B.E. Sumpio, A.C. Cordova, D.W. Berke-Schlessel, F. Qin, Q.H. Chen, J. Am. Coll. Surg. 202 (2006) 813–820.
[46] A. Gałuszka, P. Konieczka, Z.M. Migaszewski, J. Namieśnik, TrAC 37 (2012) 61–72.