Research article

Surfactant-coupled titanium dioxide coated iron-aluminium mixed metal hydroxide for magnetic solid phase extraction of bisphenols in carbonated beverages

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ABSTRACT

In this work, the magnetic sorbents based on different surfactant-coupled titanium dioxide coated iron-aluminium mixed metal hydroxide were investigated as sorbent for extraction of bisphenol compounds. The structure, morphology, and magnetic property of the synthesized sorbents were investigated. The cetyltrimethylammonium bromide-titanium dioxide coated iron-aluminium mixed metal hydroxide (Fe–Al MMH@TiO$_2$-CTAB) exhibited excellent extraction performance toward bisphenols and was selected as the sorbent for development of magnetic solid phase extraction (MSPE) method. The entire MSPE process was optimized, and the extract was analyzed by high performance liquid chromatography with photodiode array detector. The method provided wide linear calibration ranges for bisphenols between 0.3–6000 µg L^{-1} with maximum enrichment factors of 280. The limits of detection and limits of quantification were in the ranges of 0.08–0.3 and 0.3–1.0 µg L^{-1}, respectively. The proposed MSPE method was tested for determination of bisphenols in carbonated beverages. The studied carbonated beverages were mostly free of bisphenol contamination; however, BPS, BPA and BPB were detected in samples taken from defective cans. The relative recoveries ranging of 80.2–118.9% were obtained. The as-prepared Fe–Al MMH@TiO$_2$-CTAB sorbent provided high sorption capacities in the range of 2215–2451 mg kg^{-1} and could be a promising material for bisphenols in beverage samples.

1. Introduction

Bisphenols are organic chemical compounds extensively used in a wide variety of consumer products. Bisphenol A (BPA) is primarily used in the manufacturing of polycarbonate, epoxy resins i.e. in the production of food-contact surface lacquers for cans [1, 2]. BPA can leach from interior can coating or polycarbonate containers into food due to acidic conditions or thermal treatment in processing [3]. BPA and its structural-like chemicals or derivatives, such as bisphenol B (BPB), bisphenol C (BPC), bisphenol F (BPF), bisphenol S (BPS), bisphenol Z (BPZ), bisphenol AP (BPAP), bisphenol AF (BPAF), and bisphenol diglycidyl ethers (BDGEs), are classified as endocrine disrupting compounds (EDCs). Several studies have shown that these compounds have potential risk on physical health and interfere hormone systems of both animal and human [4, 5]. Due to their extensive uses and the hazards associated with them, the determination of these emerging contaminants requires the innovative development of effective and robust analytical approaches to control human exposure.

The analytical techniques for quantification of bisphenols in food and beverages are mostly based on chromatographic techniques i.e., gas chromatography (GC) [1], high-performance liquid chromatography (HPLC) coupled with photodiode array [2, 3, 4], fluorescence [5], and ultra-high performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) [6, 7]. A derivatization step is generally required to improve the volatility of the compounds in GC analysis [1]. Several HPLC conditions offered an efficient separation of some bisphenols in their nature forms [2, 3, 4]. Sample clean-up and enrichment methods are recommended prior to instrumental analysis to enhance the sensitivity and obtain accurate results. In this respect, magnetic solid phase extraction (MSPE) represents one of versatile sample pretreatment methods for extracting trace bisphenols in various matrices [2, 3, 5, 8, 9, 10, 11, 12, 13]. MSPE is carried out by direct dispersion of the magnetic sorbents in a sample solution, and the sorbent materials adsorb the

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intended analytes after incubation for a certain time. The magnetic sorbent is collected by applying an external magnetic field, and after elution with an appropriate solvent, the concentrated analyte in the extract is subsequently analyzed [14, 15]. MSPE has superior advantages comparing with other sorbent-based extraction techniques, including reduction of the extraction time, less consumption of hazardous organic solvents, and simple and fast isolation of the sorbent using an external magnet.

Different MSPE sorbents has been introduced for the extraction of bisphenols, including magnetic activated carbon [3], magnetic graphene hybrid materials [4, 5, 8], magnetic covalent organic framework [10], molecularly imprinted magnetic nanoparticles [11], and ionic liquid coated magnetic core-shell nanoparticles [13]. Recently, mixed metal hydroxide (MMH) is attractive magnetic material with high structural stability and strong magnetic property. However, surface modification of the magnetic materials is required to avoid the interparticle aggregation and improve the sorption capability toward the target analytes. Various coating materials have been proposed to modify the magnetic surface. Silica is promising material for use as inorganic outer-layer as its functionalization is well developed for various application purposes [16]. Titania or titanium dioxide (TiO_2) is become an effective sorbent with high sorption capacity capable for both cations and anions [17]. Due to its high surface homogeneity, TiO_2 has a high selectivity for a large variety of compounds and has shown potential applications in adsorption [17, 18] and separation science [19]. Modification of metal oxide materials by the surfactant can also greatly improve their sorption ability for the target compounds [20, 21, 22]. Surfactants can form self-aggregates on solid surfaces and the aggregation forms are influenced by surfactant concentration.

Surfactant-coupled TiO_2-modified material has attracted more attention due to the synergistic effect of both TiO_2 and surfactant, including good adsorption ability, dispersibility, chemically and thermodynamically stable, non-toxic, and environmentally friendly [23, 24, 25, 26]. The aim of this work was to fabricate an efficient sorbent for application in MSPE method. Iron-aluminium mixed metal hydroxide (Fe–Al MMH) was used as magnetic material. TiO_2 coupled with different kinds of surfactants, including anionic surfactant, cationic surfactant, and non-ionic surfactant, were investigated as modified agents on the magnetic materials. The structures, morphologies, and specific properties of the synthesized sorbents were investigated. The adsorption capability of each sorbent toward bisphenols was evaluated. Four predominant bisphenols extensively used in polymer production, including BPA, BPB, BPC, and BPS were selected as target analytes. The studied sorbent provided high sorption efficiency, Fe–Al MMH@TiO_2-CTAB, was selected for development of MSPE for bisphenols before analysis by HPLC coupled with photo diode array (PDA) detector. The extraction conditions were studied. The developed MSPE method has been validated and applied to the determination of bisphenols in carbonated beverages.

2. Experimental

2.1. Chemicals

The analytical reagent grade chemicals were used in the present work. These included $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Carlo Erba (Milan, Italy), $AlCl_3 \cdot 6H_2O$ (QRëC, Auckland, New Zealand), H_3PO_4 (QRëC, Auckland, New Zealand), CH_3COOH (Carlo Erba, Val de Reuil, France), and NaOH (Merck, Darmstadt, Germany). Sodium tetraborate and boric acid were received from KemAus (New South Wales, Australia). Cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were obtained from Ajax Finechem Pty Ltd (Auckland, New Zealand). Titanium (IV) isopropoxide was supplied by Acros (Geel, Belgium). Polyoxyethylene sorbitol ester or Tween 20 (TW20) and polyethylene glycol tert-octylphenyl ether or Triton-X100 (TX100) were purchased from Panreac (Bacelona, Spain) and Sigma-Aldrich (Steinheim, Germany), respectively. The solvents used in the present work involved

methanol (Merck, Darmstadt, Germany), acetone (ANaPure, Hong Kong), ethyl acetate (QRëC, Auckland, New Zealand), and HPLC grade acetonitrile (Merck, Darmstadt, Germany). (All bisphenol standards with a purity above 99% were used. BPS, BPA, and BPB were purchased from Dr. Ehrenstorfer (Augsburg, Germany). BPC was purchased from Sigma-Aldrich (Buchs, Switzerland). Stock standard solution (1000 mg L^{-1}) of each bisphenol was prepared in methanol. Working solutions were freshly prepared by diluting the stock standard solution with water. Deionized water with resistivity of 18.2 MΩ·cm was used throughout the experiments (Simplicity® ultrapure water system Type 1, Millipore, Darmstadt, Germany).

2.2. Apparatus

A Perkin Elmer Spectrum One FTIR spectrometer was used for studying the functional groups of the synthesized materials. The Fourier transform infrared (FTIR) spectra based on a standard KBr disk method were recorded between 400 and 4000 cm^{-1}. The crystal structure, morphology, and size of the synthesized materials were studied using a PANalytical, EMPYREAN X-ray diffractometer (XRD) using monochromatic Cu Kα radiation ($\lambda = 0.15406$ nm) in the 2θ range of 10°–80°, a scanning electron microscope (FEI Helios NanoLab G3 CX DualBeam FIB/SEM), and a transmission electron microscope (FEI Tecnai G^2 20 TEM) coupled with energy dispersive X-ray analysis (EDX) operating at a voltage of 200 kV. A vibrating sample magnetometer (Lake Shore VSM 7403), operated at 298 K and ±10000 Oersted (Oe) applied magnetic field (H), was used for studying the magnetic properties. The surface area and pore size analyzer model BELSORP - mini X (MicrotracBEL Corp., Japan) was used for measurement of the specific surface area of the material.

Chromatographic separation was carried out using HPLC with PDA detector (Waters 2996, Waters, USA). The system was equipped with a 10-μL sample loop, an ACE 5 C18 column (4.6 mm × 250 mm, 5 μm, Advanced Chromatography Technologies Ltd.), and an Empower software for recording the chromatographic data. Separation was performed using an isocratic mode of 57% acetonitrile and 43% acetic acid (0.1% v/v) as mobile phase, and a flow rate of 1.0 mL min^{-1}. Detection of the target analytes was performed simultaneously at 259 nm for BPS, and 278 nm for BPA, BPB, and BPC.

2.3. Synthesis of Fe–Al MMH@TiO_2-CTAB sorbents

Synthesis of Fe–Al MMH based on co-precipitation method was carried out. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (5 mmol) and $AlCl_3.6H_2O$ (2.5 mmol) were dissolved in water (100 mL). Then, 20 mL of NaOH (3 mol L^{-1}) was immediately added into the solution and stirred vigorously for 10 min under closed system. The black powder of Fe–Al MMH was magnetically collected, and sequentially washed with water and methanol.

The proposed magnetic sorbent was prepared by a surfactant-involved sol–gel process. As-prepared Fe–Al MMH was re-dispersed in methanol (95 mL). Then, CTAB (1 g) was subsequently introduced and stirred for 30 min. Next, 1 mL of titanium (IV) isopropoxide was added dropwise and the mixture was stirred for 1 h. Deionized water (5 mL) was subsequently introduced and kept stirring for 3 h. The reaction was stored in an ice bath. The solid sorbent, defined as Fe–Al MMH@TiO_2-CTAB, was washed with methanol, and dried in an oven at 80 °C. Other studied magnetic sorbents, Fe–Al MMH@TiO_2-SDS, Fe–Al MMH@TiO_2-TW20, and Fe–Al MMH@TiO_2-TX100 were also synthesized in the same manner as described above but using different types of surfactants, involving SDS, TW-20, and TX-100, respectively.

2.4. Proposed MSPE procedure

In the present work, the Fe–Al MMH@TiO_2-CTAB sorbent was employed for development of the MSPE procedure for bisphenol compounds. The experimental process was started by adding 50 mg magnetic
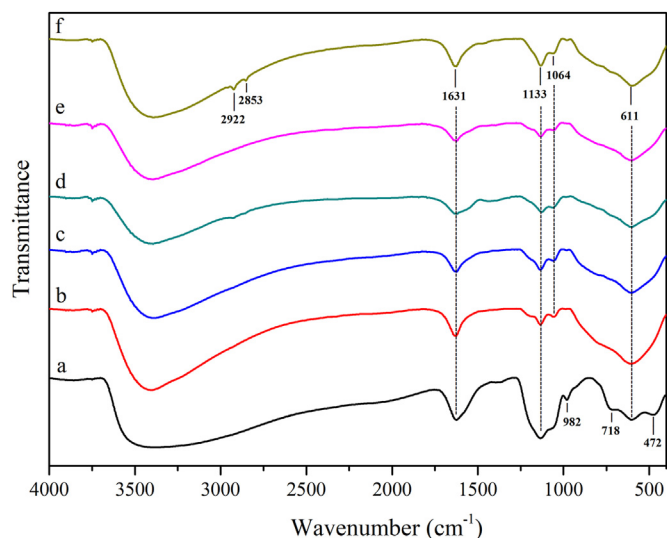
Figure 1. FTIR spectra of (a) Fe–Al MMH, (b) Fe–Al MMH@TiO$_2$, (c) Fe–Al MMH@TiO$_2$-SDS, (d) Fe–Al MMH@TiO $_2$-TW20, (e) Fe–Al MMH@TiO$_2$-TX100 and (f) Fe–Al MMH@TiO$_2$-CTAB

sorbents into a sample solution (20 mL). A vigorous vortexing was applied for 45 s to accelerate dispersion of the sorbent. The target analytes were retained on the magnetic sorbents in this step. Next, the sorbent was collected by placing an external magnet on the outside of the extraction vessel before discarding the supernatant. Acetonitrile (1 mL), as the desorption solvent, was added to desorb the target analytes from the sorbents with the vortex desorption time of 90 s. The sorbents were then magnetically isolated within 20 s, and the collecting solution was filtered through a 0.45-μm nylon membrane filter. The extract was further concentrated through evaporation under N$_2$. The residue was redissolved in 50 μL acetonitrile before being analyzed by HPLC-PDA.

2.5. Sample collection and preparation

Five canned carbonated beverages, including sugar free lemon-lime soda, lemon soda, sugar free lemon soda, tonic water, and sugar free cola, purchased from the convenience stores in Khon Kaen province, Thailand, were taken as samples. Two samples, including sugar free cola

Figure 2. XRD patterns of (a) Fe–Al MMH, (b) Fe–Al MMH@TiO$_2$, (c) Fe–Al MMH@TiO$_2$-SDS, (d) Fe–Al MMH@TiO $_2$-TW20, (e) Fe–Al MMH@TiO$_2$-TX100, (f) Fe–Al MMH@TiO$_2$-CTAB

and sparkling water soda, taken from defective cans were also determined. Before analysis, the samples were degassed for 30 min using ultrasonic bath, and the pH was adjusted to 8.0 using 0.1 mol L^{-1} borate buffer solution.

2.6. Validation of the MSPE method

To evaluate the analytical performance of the proposed MSPE method, the validation parameters, including linearity, limits of detection (LODs), limits of quantification (LOQs), enrichment factors (EFs), and precision, were studied under optimized conditions. The LODs and LOQs were investigated according to the concentrations giving the signal-to-noise (S/N) ratios of 3 and 10, respectively. The EFs were calculated based on the ratio of the analyte concentrations obtained by MSPE and the initial concentration. The method precisions were determined in terms of intraday (n = 5) and interday (n = 5 × 3) relative standard deviations (RSDs) using bisphenol concentration at 2000 μg L^{-1} each. To examine the recovery, bisphenols at different concentrations (5, 50, and 500 μg L^{-1}) were spiked into the beverage samples before being analyzed by the proposed MSPE-HPLC method.

3. Results and discussion

3.1. Material characterization

The FTIR spectra were recorded to identify the functional group of the synthesized materials, as shown in Figure 1. The large broad band in the range of 3200–3600 cm^{-1} exhibited the stretching vibration of the –OH in MMH, while the vibration peak at 1631 cm^{-1} relating to –OH bending vibration of water molecules was also observed. The small peaks below 800 cm^{-1} corresponded to the metal-oxygen stretching and bending modes of MMH [27]. In Figure 1(b–f), the additional weak Fe–O–Ti vibration located at 1064 cm^{-1}, and the vibration broad band around 400–900 cm^{-1} relating to the Ti–O–Ti vibration were observed. The vibration peak at 611 cm^{-1} due to the metal-oxygen vibration of Fe–Al MMH was existed with low intensity [20, 26, 28]. In addition, two weak absorption bands at 2922 and 2853 cm^{-1} were observed in Fe–Al MMH@TiO$_2$-CTAB (Figure 1(f)), which assigned to the asymmetric and symmetric stretching vibrations of CH$_2$ in long alkyl chains of CTAB, respectively [20, 29].

XRD patterns of the as-prepared magnetic sorbents are presented in Figure 2. The diffraction pattern of Fe–Al MMH in Figure 2(a) exhibited peaks with 2θ values of 30.4°, 35.8°, 53.7°, 57.5° and 63.1°, assigning to
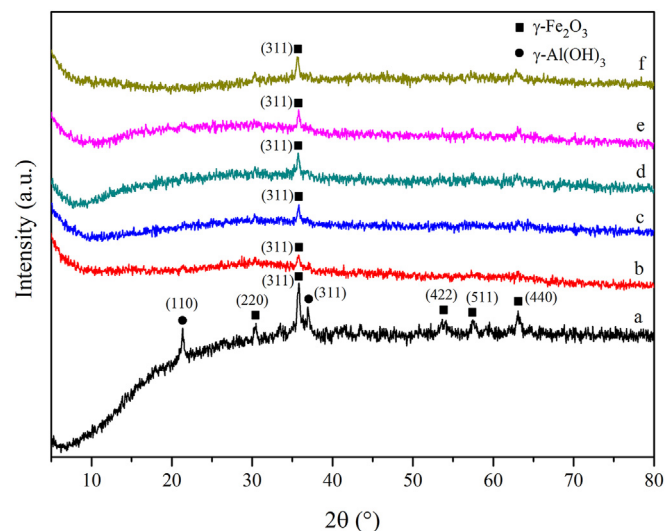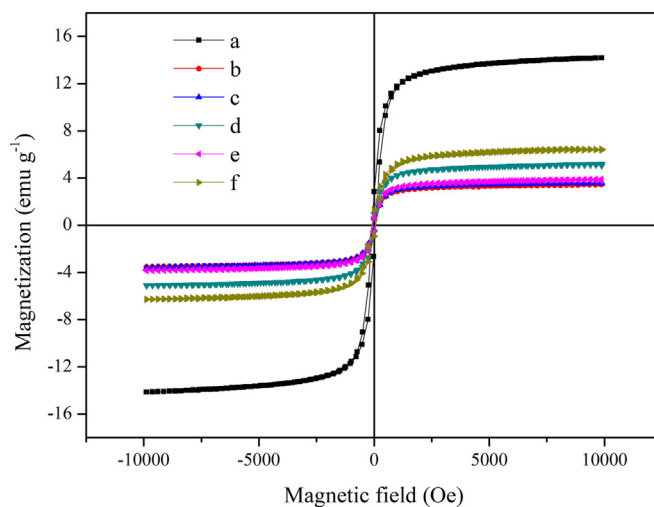

Figure 3. Magnetic property of (a) Fe–Al MMH, (b) Fe–Al MMH@TiO$_2$, (c) Fe–Al MMH@TiO$_2$-SDS, (d) Fe–Al MMH@TiO$_2$-TW20, (e) Fe–Al MMH@TiO$_2$-TX100 and (f) Fe–Al MMH@TiO$_2$-CTAB

Table 1. Analytical performance of the proposed MSPE method for determination of bisphenols.

Analyte	Linear range ($\mu g\ L^{-1}$)	Linear equation	R^2	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	EF	Q_{max} (mg kg^{-1})	RSD (%) Intraday (n = 5)	RSD (%) Interday (n = 5 × 3)
BPS	0.3–6000	$y = 8416.4x + 32409$	0.9908	0.08	0.3	172	2215	2.3	5.6
BPA	1.0–6000	$y = 2579.3x + 12905$	0.9939	0.3	1.0	240	2419	1.1	5.9
BPB	1.0–6000	$y = 2269.1x + 10771$	0.9949	0.3	1.0	272	2451	3.4	7.1
BPC	1.0–6000	$y = 2974.6x + 17476$	0.9940	0.3	1.0	280	2432	3.9	5.9
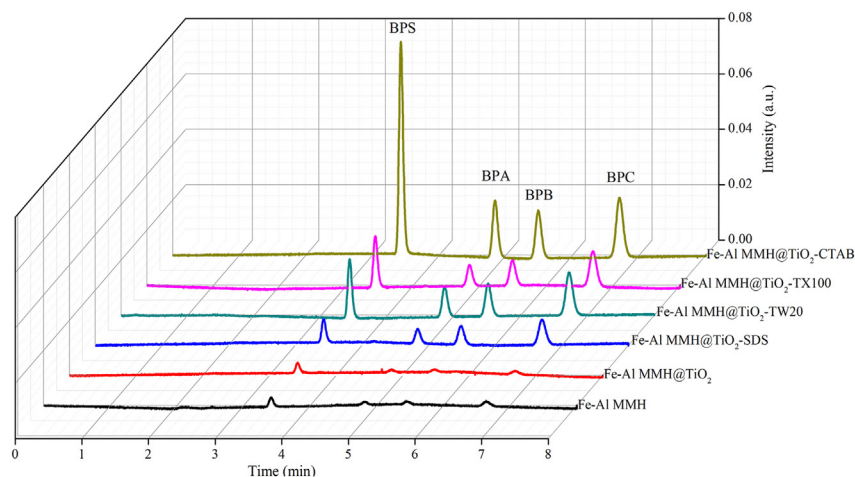
Figure 4. Chromatograms of bisphenols obtained from MSPE using different magnetic sorbents.

(220), (311), (422), (511) and (440) crystal planes of Fe_2O_3, respectively. The diffraction peaks at 21.3° and 36.8° due to the crystal planes of (110) and (311), respectively, were clearly observed, which confirmed the existence of γ-Al(OH)$_3$ phase. All diffraction peaks could be attributed to the mixture of crystallinity of γ-Fe_3O_4 and γ-Al(OH)$_3$, which related to JCPDS card no. 39-1346, and JCPDS card no. 7-0324, respectively. After modifying the surface with different surfactants and TiO_2, only low intensity peak at 2θ of 35.8° was found (Figure 2(b–f)). These could be due to obstruction by the amorphous phases of surfactants and TiO_2 [30–31]. The EDX spectra in Figure S1(a), in Supplementary Material, showed the composition of Fe, Al and O in structure of Fe–Al MMH with the weight percentages of 48.91%, 7.83%, and 43.24%, respectively. The inset of Figure S1(a) clearly depicted crystal planes of Fe–Al MMH. The EDX results in Figure S1(b) confirmed the existence of TiO_2 layer on Fe–Al MMH surface, with the weights of 26.57%, 6.21%, 42.39%, and 24.80% for Fe, Al, O, and Ti, respectively. The inset of Figure S1(b) also confirmed the appearance of TiO_2 on the Fe–Al MMH surface.

Figure S2 (Supplementary Material) showed the SEM micrographs of as-prepared sorbents. The Fe–Al MMH exhibited an aggregation of spherical-like shape with an average particle size of 58 ± 2 nm (Figure S2(a)). The SEM micrographs in Figure S2(b–e) showed spherical-like shape of Fe–Al MMH@TiO_2, Fe–Al MMH@TiO_2-SDS and Fe–Al MMH@TiO_2-TX100, and rod-like shape of Fe–Al MMH@TiO_2-TW20. The mixed rod- and sheet-like shape were observed in Fe–Al MMH@TiO_2-CTAB (Figure S2(f)). The mixed morphology and a large particle size of Fe–Al MMH@TiO_2-CTAB corresponded to the orientation of CTAB around Fe–Al MMH magnetic core. The estimated particle sizes of 151 ± 5, 128 ± 6, 105 ± 5, 117 ± 7, and 196 ± 7 nm were observed for Fe–Al MMH@TiO_2, Fe–Al MMH@TiO_2-SDS, Fe–Al MMH@TiO_2-TW20, Fe–Al MMH@TiO_2-TX100 and Fe–Al MMH@TiO_2-CTAB, respectively.

TEM micrographs of the magnetic sorbents were illustrated in Figure S3 (Supplementary Material). Type of surfactant could affect the formation of coating layer, resulting in diverse shell thicknesses. The shell thicknesses of Fe–Al MMH coated with TiO_2 and different surfactants were about 21, 17, 9, 14, and 26 nm for Fe–Al MMH@TiO_2, Fe–Al

MMH@TiO_2-SDS, Fe–Al MMH@TiO_2-TW20, Fe–Al MMH@TiO_2-TX100 and Fe–Al MMH@TiO_2-CTAB, respectively. Interestingly, the TiO_2 structures not provided only the feature as protecting layer on Fe–Al MMH, but also exhibited porous among them, suggesting enhancement of surface area and surface interacting sites toward surfactant. Therefore, these results also supported the successful coating of surfactant-coupled TiO_2 on Fe–Al MMH.

The M-H curves of synthesized sorbents are shown in Figure 3. The saturated magnetization and hysteresis loop were observed for all studied sorbents, indicating the ferromagnetic behavior. The magnetization values of 14.19, 3.52, 3.62, 5.21, 3.90, and 6.43 emu g^{-1} were obtained for Fe–Al MMH, Fe–Al MMH@TiO_2, Fe–Al MMH@TiO_2-SDS, Fe–Al MMH@TiO_2-TW20, Fe–Al MMH@TiO_2-TX100 and Fe–Al MMH@TiO_2-CTAB, respectively. Compared to Fe–Al MMH, decreasing of the
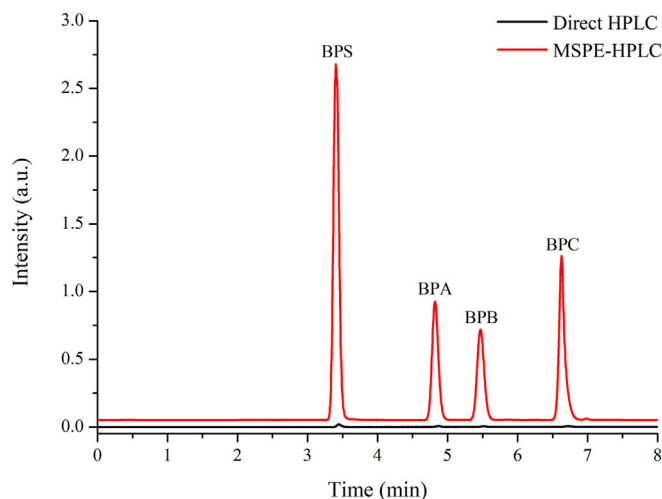
Figure 5. Chromatograms of bisphenols obtained from direct HPLC-PDA analysis and after preconcentration by MSPE method.

magnetization values of the modified sorbents were possibly explained by diamagnetic shielding effect. Although the surfactant-TiO$_2$ coated Fe–Al MMH significantly exhibited lower magnetic power, those magnetic strengths were sufficient for application in MSPE process.

The synthesized ferromagnetic Fe–Al MMH acted as magnetic core and provided sufficient magnetic strength for collection by the external magnet during MSPE process. Addition of CTAB could provide large interaction sites toward the target analytes leading to the excellent extraction efficiency [32]. In addition, CTAB can also improve the stability of the magnetic material in aqueous solution and facilitate the TiO$_2$ layer arranging on Fe–Al MMH [33]. TiO$_2$ provides high surface area and protects Fe–Al MMH surface from oxidation [34, 35]. The surface area of the sorbents was measured and calculated by Brunauer-Emmett-Teller method. High specific surface area of 331.09 m^2 g^{-1} was obtained for Fe–Al MMH@TiO$_2$-CTAB, which was larger than that obtained from individual Fe–Al MMH (70 m^2 g^{-1}). These could verify the feature of TiO$_2$ coating layer.

The ability of the Fe–Al MMH@TiO$_2$-CTAB sorbent to adsorb bisphenols (concentration range: 2000–8000 μg L^{-1}) was investigated under optimized extraction conditions. The maximum sorption capacity is calculated using equation Q$_{max}$ = (C$_i$ - C$_f$)V/m, where Q$_{max}$ is maximum sorption capacity of the sorbent (mg kg^{-1}), C$_i$ and C$_f$ are the initial and final concentrations of bisphenols (μg L^{-1}), respectively, V is volume of the sample (L), and m is amount of Fe–Al MMH@TiO$_2$-CTAB sorbent (g). The as-prepared Fe–Al MMH@TiO$_2$-CTAB magnetic sorbent exhibited superior sorption capacities of 2215–2451 mg kg^{-1} toward bisphenols, as summarized in Table 1. The highest sorption capacity was obtained for BPB due to its higher log K$_{ow}$ (4.13) comparing to other bisphenols, while the lowest sorption capacity was found in BPS, corresponded to its low log K$_{ow}$ (1.65). It could be explained that the analytes having larger log K$_{ow}$

preferred to leave the aqueous phase, and the hydrophobic interaction was readily driven between hydrophobic site of bisphenols and hydrophobic tail of CTAB on the sorbent [36, 37, 38]. In addition, dipole-dipole interaction possibly occurred from positively charged CTAB species on the sorbent and electron-donating hydroxyl group of bisphenols [39].

3.2. Optimization of MSPE condition

In this work, different surfactants were studied for modifying Fe–Al MMH@TiO$_2$ sorbent, including SDS, TW20, TX100, and CTAB. The extraction efficiency of each surfactant-modified magnetic sorbents toward bisphenols were investigated under the controlled conditions: 50 mg sorbent, sample volume (10 mL, pH 6.8), 60 s vortex times during adsorption and desorption, and acetonitrile (1 mL) as desorption solvent. As illustrated in Figure 4, the magnetic sorbents modified with surfactant provided higher extraction ability for the target analytes. Type of surfactant also significantly influenced the extraction efficiency. In particular, the Fe–Al MMH@TiO$_2$-CTAB exhibited the highest extraction performance for all studied bisphenols. This could be due to CTAB favorably arranged on the surface of Fe–Al MMH@TiO$_2$ and served as active sites toward bisphenols through electrostatic attraction between cationic head groups in CTAB and anionic hydroxyl in bisphenols. Therefore, Fe–Al MMH@TiO$_2$-CTAB was adopted as sorbent for MSPE of bisphenols in this work.

The effect of the amount of Fe–Al MMH@TiO$_2$-CTAB sorbent was investigated in the range of 5–90 mg, while other parameters were set as follows: sample solution (10 mL, pH 6.8), 60 s vortex adsorption and desorption times, and acetonitrile (1 mL) as desorption solvent. Figure S4 (Supplementary Material) revealed that the peak areas of analytes increased as the sorbent amounts were increased from 5 to 50 mg, and

Table 2. Determination of bisphenols in carbonated beverages by the proposed MSPE-HPLC method.

Samples	BPS	BPA	BPB	BPC
Sugar free lemon-lime soda, found (μg L^{-1})	–	–	–	–
%R1 (%RSD)	81.8 (4.9)	88.4 (5.7)	86.2 (1.6)	83.8 (5.7)
%R2 (%RSD)	114.3 (0.4)	101.5 (5.8)	107.7 (5.1)	81.6 (3.0)
%R3 (%RSD)	80.4 (0.2)	85.1 (3.7)	86.2 (2.6)	94.9 (2.9)
Lemon soda, found (μg L^{-1})	–	–	–	–
%R1 (%RSD)	82.6 (1.2)	114.8 (4.1)	117.2 (1.9)	80.2 (3.4)
%R2 (%RSD)	100.2 (2.2)	118.8 (3.4)	86.3 (5.8)	116.3 (6.5)
%R3 (%RSD)	80.3 (3.0)	82.0 (2.2)	84.2 (5.6)	116.3 (1.3)
Sugar free lemon soda, found (μg L^{-1})	–	–	–	–
%R1 (%RSD)	80.8 (5.7)	112.3 (9.5)	102.8 (9.2)	95.7 (6.6)
%R2 (%RSD)	113.8 (6.2)	115.4 (3.2)	94.1 (6.4)	117.2 (3.7)
%R3 (%RSD)	87.5 (9.2)	99.1 (7.3)	84.5 (6.2)	118.9 (9.6)
Tonic water, found (μg L^{-1})	–	–	–	–
%R1 (%RSD)	91.4 (3.1)	104.5 (6.6)	106.5 (5.7)	116.3.0 (3.3)
%R2 (%RSD)	85.1 (2.5)	87.0 (2.8)	112.9 (1.4)	118.8 (1.2)
%R3 (%RSD)	88.1 (3.1)	85.1 (3.1)	87.6 (4.4)	102.1 (3.0)
Sugar free cola 1, found (μg L^{-1})	–	–	–	–
%R1 (%RSD)	117.3 (6.3)	98.8 (6.9)	98.8 (9.1)	84.7 (4.3)
%R2 (%RSD)	110.1 (4.4)	108.9 (1.9)	97.3 (6.0)	84.3 (2.3)
%R3 (%RSD)	107.5 (5.2)	82.2 (5.0)	84.0 (1.1)	82.2 (2.3)
Sugar free cola 2[a], found (μg L^{-1})	<LOQ	1.46	1.39	–
%R1 (%RSD)	96.4 (2.8)	100.7 (9.9)	86.6 (8.6)	101.9 (8.2)
%R2 (%RSD)	102.3 (5.9)	98.5 (9.3)	97.2 (5.9)	83.4 (2.5)
%R3 (%RSD)	107.5 (5.2)	82.2 (5.0)	84.0 (1.1)	82.2 (2.3)
Sparkling water soda[a], found (μg L^{-1})	<LOQ	<LOQ	<LOQ	–
%R1 (%RSD)	108.5 (0.5)	86.7 (6.1)	87.3 (1.3)	94.3 (9.1)
%R2 (%RSD)	105.9 (2.9)	95.3 (3.8)	87.8 (6.3)	83.2 (2.6)
%R3 (%RSD)	115.1 (6.7)	113.9 (1.3)	83.1 (1.0)	92.5 (0.9)

– Not detected refers to values below LODs.
Spiked concentrations: R1, 5 μg L-1; R2, 50 μg L-1; R3, 500 μg L-1.
[a] Samples taken from defective cans.

Table 3. Comparison of validation data for analysis of bisphenols with other MSPE methods.

Sorbent [Ref]	Analytes	Sample matrix	MSPE condition	Analytical performance
Fe_3O_4-graphene@ polydopamine-zirconium MOFs [2]	BPF, BPA, BPB, BPAP, BPAF	Environmental samples	Sorbent: 30 mg Sample: 10 mL Adsorption: 10 min Desorption: 15 min, 1 mL acetonitrile	Linear range: 50–20,000 µg L^{-1} LODs: 0.1–1.0 µg L^{-1} LOQs: 0.33–3.3 µg L^{-1} RSD: ≤4.89% %R: 64.8–92.8
Fe_3O_4-impregnated activated carbon [3]	BPA	Milk	Sorbent: 5 mg Sample: 1 g Adsorption: 15 min Desorption: 15 min, 500 µL methanol:acetonitrile (1:1 v/v)	Linear range: 2.5–5000 µg kg^{-1} LOD: 0.75 µg kg^{-1} LOQ: 2.5 µg kg^{-1} RSD: ≤3.7% %R: 89.1–99.4 Q_{max}: 353.39 mg g^{-1}
Ni@N-doped graphene tubes [5]	BPA, BPB, BPAP, BPAF	Milk	Sorbent: 5 mg Sample: 5 mL, pH: 5.6 Extraction: 6.3 min Desorption: 5 min, 2 mL acetone, dried and redissolved in50 µL methanol	Linear range: 0.33–500 µg L^{-1} LODs: 0.10–0.20 µg L^{-1} LOQs: 0.33–0.66 µg L^{-1} RSD: ≤6.78% %R: 83.6–105.1
Graphene/$ZnFe_2O_4$ composite [8]	BPS, BPF, BPA, BPAF, BPAP, TDP, BPC, TCBPA, TBBPA	Water	Sorbent: 60 mg Sample: 400 mL, pH 5.6 Adsorption: 15 min Desorption: 2 min, 2.0 mL of acetonitrile–0.2% NaOH, dried and redissolved in 500 µL methanol	Linear range: 0.5–500 ng mL^{-1} MDLs: 0.05–0.18 ng mL^{-1} MQLs: 0.15–0.59 ng mL^{-1} RSD: ≤6.2% %R: 95.1–103.8 EFs: 800
Fe@SiO_2@poly (N-isopropylacrymide -co-methacrylic) [9]	BPA, phenol, hydroquinone	Water	Sorbent: 40 mg Sample: 100 mL, pH 5 Adsorption: 40 min Desorption: 3 mL methanol, dried and redissolved in 200 µL methanol	Linear range: 0.1–500 µg L^{-1} LODs: 0.019–0.031 µg L^{-1} RSD: ≤4.80% %R: 94.0–105.4
Fe_3O_4@covalent organic framework [10]	BPS, BPF, BPA, BPB, BPAF	Human serum	Sorbent: 20 mg Sample: 50 mL, pH 7 Extraction: 10 min Desorption: 2 min, 1.5 mL i-propanol, dried and redissolved in 100 µL water	Linear range: 0.1–50 µg L^{-1} LODs: 1.0–78.1 ng L^{-1} LOQs: 3.2–260.3 ng L^{-1} RSD: ≤6.9% %R: 93.0–107.8 EFs: 56–95
Fe_3O_4@SiO_2 @nylon-6 [12]	BPA	Milk	Sorbent: 80 mg Sample: 5 mL Extraction: 30 min Desorption: 0.5 mL methanol, dried and redissolved in 50 µL methanol	Linear range: 10.2–4000 µg L^{-1} LOD: 3.05 µg L^{-1} LOQ: 10.16 ng L^{-1} RSD: ≤7% %R: 86–99
Fe_3O_4@SiO_2 @ionic liquid [13]	BPA	Plastic tableware	Sorbent: 100 mg Sample: 100 mL, pH 7 Extraction: 10 min, 35 °C Ionic strength: 20 % NaCl Desorption: 15 °C, 5 min, 4 mL methanol	Linear range: 0.5–20,000 µg L^{-1} LODs: 0.09 µg L^{-1} RSD: ≤1.2% %R: 99.6–100.6 EF: 25 Q_{max}: 6.06 mg g^{-1}
Fe_3O_4@carbon @chitosan [41]	BPA	Aqueous samples	Sorbent: 20 mg Sample: 5 mL Adsorption: 20 min Desorption: 1 mL methanol	Linear range: 0.1–50 µg L^{-1} LODs: 1.0–78.1 ng L^{-1} LOQs: 3.2–260.3 ng L^{-1} RSDs: ≤6.9% %R: 93.0–107.8 EFs: 56–95
Fe–Al MMH @TiO_2-CTAB [This work]	BPS, BPA, BPB, BPC	Carbonated beverages	Sorbent: 50 mg Sample: 20 mL, pH 8 Adsorption: 45 s Desorption: 90 s, 1 mL acetonitrile, dried and redissolved in 50 µL acetonitrile	Linear range: 0.3–6000 µg L^{-1} (BPS), 1–6000 µg L^{-1} (BPA, BPB, BPC) LODs: 0.08–0.3 µg L^{-1} LOQs: 0.3–1.0 µg L^{-1} RSD: ≤7.1% %R: 80.2–118.9 EFs: 172–280 Q_{max}: 2215–2451 mg kg^{-1}

then slightly decreased afterward. Therefore, 50 mg of Fe–Al MMH@TiO$_2$-CTAB was chosen for subsequent experiments.

During the MSPE process, vortex agitation was applied to enhance the degree of dispersion for the extraction and desorption. The vortex time during desorption of the analytes from the sorbent was investigated from 30 to 150 s, using 50 mg Fe–Al MMH@TiO$_2$-CTAB sorbent, 10 mL sample solution at pH 6.8, vortex adsorption time of 60 s, and acetonitrile (1 mL) for desorption. The peak areas of analytes slightly increased with increasing vortex time from 15 to 90 s (data not shown), suggesting that desorption equilibrium was reached at 90 s. Therefore, vortex desorption time of 90 s was adopted for this work.

The vortex adsorption time was also varied in the range of 15–90 s, using 50 mg Fe–Al MMH@TiO$_2$-CTAB sorbent, 10 mL sample solution at pH 6.8, 90 s desorption time, and acetonitrile (1 mL) as desorption solvent. The higher extraction efficiencies were obtained with increasing adsorption time from 15 to 45 s, and then slightly decreased (data not shown). This could be suggested that the extraction equilibrium was achieved within 45 s and it was selected for further investigation.

Suitable solvent is required for eluting the target analytes from the magnetic sorbent. In this work, different solvents, including methanol, acetone, ethyl acetate and acetonitrile, were investigated. The following MSPE conditions were controlled: 50 mg sorbent, sample solution (10 mL, pH 6.8), 45 s adsorption time, 90 s desorption time, and 1 mL desorption solvent. The results in Figure S5 (Supplementary Material) indicated that acetonitrile attained the highest elution efficiency for all bisphenols. Therefore, acetonitrile was used as desorption solvent in MSPE procedure.

To obtain high enrichment factor of MSPE process, the volume of desorption solvent (acetonitrile) was varied from 0.25 to 1.75 mL, while other parameters including 50 mg sorbent, sample solution (10 mL, pH 6.8), 45 s adsorption time, and 90 s desorption time were controlled. In addition, the collected extract was purged with a stream of N$_2$ at room temperature until dryness and the residue was reconstituted in 50 μL acetonitrile before determination. The results presented in Figure S6 (Supplementary Material) showed that the extraction efficiency of all bisphenols reached the maximum using the volume of desorption solvent of 1.0 mL. Therefore, the desorption solvent volume was selected at 1.0 mL for subsequent experiments.

The sample volume has an influence on the enrichment factor of MSPE method and was studied in the range from 5 to 35 mL, while keeping other parameter constant: 50 mg sorbent, sample pH of 6.8, 45 s adsorption time, 90 s desorption time, and acetonitrile (1.0 mL) as desorption solvent. The results shown in Figure S7 (Supplementary Material) indicated that the high extraction efficiency of all bisphenols was obtained by extracting 20 mL sample solution. Therefore, the optimized sample volume of 20 mL was chosen for further investigation.

During adsorption process, the pH of the sample solution ranging from 3 to 11 was studied in using buffer solution. Other MSPE parameters were kept as follows: 50 mg Fe–Al MMH@TiO$_2$-CTAB sorbent, 20 mL sample solution, 45 s adsorption time, 90 s desorption time, and acetonitrile (1 mL) as desorption solvent. The results were presented in Figure S8 (Supplementary Material). The maximum extraction efficiencies of all bisphenols were attained at sample pH of 8. Therefore, the buffer solution at pH 8 was used to control the sample pH in the MSPE procedure.

3.3. Method validation

The developed MSPE method provided linear calibration graphs in the range of 0.3–6000 μg L^{-1} for BPS, and 1.0–6000 μg L^{-1} for BPA, BPB, and BPC, with coefficients of determination (R^2) varied from 0.9908 to 0.9949. The obtained LODs were 0.08 μg L^{-1} for BPS, and 0.3 μg L^{-1} for BPA, BPB, and BPC. The LOQ values were 0.3 μg L^{-1} for BPS, and 1.0 μg L^{-1} for BPA, BPB, and BPC. The EFs of 172, 240, 272, and 280 were reached for BPS, BPA, BPB, and BPC, respectively. The chromatograms of bisphenols obtained from direct HPLC and after enrichment using the proposed MSPE are presented in Figure 5. The method precisions (RSDs) of intra- and interday experiments were achieved in the ranges of 1.1–3.9

%, and 5.6–7.1 %, respectively. The validation data of the proposed MSPE procedure are summarized in Table 1.

3.4. Determination of bisphenols in beverages by the proposed MSPE method

The proposed MSPE method using Fe–Al MMH@TiO$_2$-CTAB sorbent was applied for determine bisphenols in canned beverages. The examined beverages were mostly free of bisphenol contamination, confirming the stability or non-contamination of epoxy coated on can container. However, two beverages taken from defective cans were also determined by the proposed MSPE-HPLC method. BPA and BPB were detected at 1.46 and 1.39 μg L^{-1}, respectively, in sugar free cola from defective container, which lower than the specific migration limit (0.6 mg kg^{-1} of food) regulated by the European Commission [40]. In addition, BPA, BPB, and BPS residues also presented in sparkling water soda but at concentrations lower than the LOQs. The results suggested the possible migration of bisphenol residues from can coatings under improper storage condition or transportation. Spiked samples were also analyzed, and the acceptable relative recoveries were obtained from 80.2 to 118.9% with the RSDs better than 9.9% (Table 2).

3.5. Comparison of the developed method with other reported methods

The performance of the MSPE-HPLC method based on Fe–Al MMH@TiO$_2$-CTAB for determination of bisphenols was compared with other previously reported MSPE methods [2, 3, 5, 8, 9, 10, 12, 13, 41]. As summarized in Table 3, the present work provides wide linear calibration curves for simultaneous determination of different bisphenol compounds. The sensitivity of the developed MSPE method (the obtained LODs and LOQs) is almost comparable to those reported using other extractants. The significant feature of the proposed extraction method is rapid. In addition, the synthesized Fe–Al MMH@TiO$_2$-CTAB sorbent has high adsorption capacity.

4. Conclusions

In this work, the Fe–Al MMH@TiO$_2$-CTAB sorbent was successfully prepared. The Fe–Al MMH@TiO$_2$ was synthesized by simple co-precipitation method followed by sol-gel process. An irregular morphology of TiO$_2$-CTAB encapsulating on magnetic core showed ferromagnetic behavior with sufficient magnetic power for application in MSPE process. The synthesized Fe–Al MMH@TiO$_2$-CTAB sorbent has high sorption capacity and was used for extraction of bisphenols in carbonated beverages before analysis by HPLC-PDA. This method provided good analytical features and offered short extraction time. Satisfactory recoveries demonstrated that the proposed Fe–Al MMH@TiO$_2$-CTAB is promising sorbent for bisphenols in beverage matrices.

Declarations

Author contribution statement

Jirasak Gamonchuang: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Rodjana Burakham: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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