



Preparation of multi-walled carbon nanotubes functionalized magnetic particles by sol–gel technology and its application in extraction of estrogens

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ABSTRACT

Magnetic silica particles coated with hydroxy-terminated multi-walled carbon nanotubes (MWCNTs–OH) were prepared by sol–gel technology, characterized and used for the convenient, rapid and efficient extraction of several estrogens (including diethylstilbestrol, estrone and estriol) in water followed by sweeping micellar electrokinetic chromatography analysis with UV detection. The results demonstrated that sol–gel technology was a feasible, simple and effective technique for the preparation of MWCNTs–OH functionalized magnetic silica particles. The factors affecting the extraction efficiency of estrogens (the pre-activation of magnetic particles, adsorption time, desorption time and the amount of elution solvent) were carefully investigated. The extraction efficiencies for diethylstilbestrol, estrone and estriol were 95.9%, 93.9%, and 52.4%, respectively, under the optimum conditions. The method detection limits for the three estrogens were less than 0.2 ng mL⁻¹. The developed method was applied for the analysis of tap water, mineral water, Pearl River water and honey.

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1. Introduction

Since the introduction of magnetic separation technology (MST) in 1909 [1], it has been established as a powerful separation approach in complex industrial processes, bio-separation, environmental and material science [2–8]. An important advantage of this technology is that the magnetic materials with adsorbed sample can be easily collected using an external magnetic field placed outside of the extraction container without additional centrifugation or filtration, which makes sampling and collection easier and faster. Solid-phase extraction (SPE) is regarded as one of the most popular sample preparation methods [9–12]. Magnetic solid-phase extraction (MSPE) is an excellent extraction method, which is a new procedure of SPE based on the use of magnetic or magnetizable adsorbents. Compared with traditional SPE procedure, MSPE is indicated as a time and labor effective separation approach [13]. The adsorbents need not be packed into the SPE cartridges like SPE and the phase separation could be conveniently made by applying an external magnetic field. MSPE combines the advantages of MST and SPE. Many functional magnetic particles have been developed and commercialized including poly (ethylene glycol)/superparamagnetic iron oxide nanoparticles [14], 3-aminopropyl triethoxysilane/magnetite@silica nanoparticles [15], gold or silver/Fe₃O₄ nanoparticles [16],

humic acid/Fe₃O₄ nanoparticles [17], etc. These particles have large surface areas and are chemically inert and mechanically robust. Recent reports showed that the functional magnetic particles have significant impact on sample extraction [18–21]. Cetyltrimethylammonium bromide-coated magnetic nanoparticles were reported for the pre-concentration of phenolic compounds from environmental water samples [18]. Octadecyl-functionalized magnetic silica particles have been applied for the determination of ergosterol in cigarettes [19], polycyclic aromatic hydrocarbons [20], and estrogens [21] in water. Chitosan-coated octadecyl-functionalized magnetite nanoparticles were prepared and applied for the extraction of perfluorinated compounds from environmental water samples [22].

Carbon nanotubes (CNTs) have been widely used in trapping and separating organic compounds since they were first found by Iijima in 1991 [23]. They exhibit excellent mechanical and thermal properties because of their unique geometric structure [23–25]. They have been used as adsorbents to effectively adsorb hydrogen [26], water soluble protein streptavidin [27], etc. Multi-walled carbon nanotubes (MWCNTs) have been characterized as superior sorbents for removing environmental contaminants, such as dioxins [28], phenols [29], phthalate esters [30] and chlorobenzenes [31], which indicated that MWCNTs have strong adsorption capacity towards hydrophobic organic pollutants. Therefore, the feasibility to fabricate MWCNTs functionalized magnetic particles using chemical modification method can be anticipated. These particles have the properties of MWCNTs and can be used as the adsorbents in MSPE for the extraction of hydrophobic organic pollutants.

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Relatively few works have been reported aiming the preparation of MWCNTs. Deng et al. [32] reported the preparation of magnetic silica nanoparticle functionalized MWCNTs via the amidation reaction between (3-aminopropyl) triethoxysilane modified magnetic particles and carboxy-terminated MWCNTs (MWCNTs-COOH) and the functionalized MWCNTs were applied for the separation of alkyl benzenes. In this study, hydroxy-terminated MWCNTs (MWCNTs-OH) were used as coating materials for the preparation of MWCNTs-OH functionalized magnetic particles based on sol-gel technique. The characterization of the magnetic MWCNTs-OH particles was studied by Raman spectrometry. The performance of the prepared particles for the extraction of hydrophobic organic pollutants was evaluated by the extraction of estrogens followed by sweeping micellar electrokinetic chromatography (MEKC) analysis. The extraction efficiencies for estrogens using magnetic MWCNTs-OH particles as adsorbents were compared to a previously published work [21] which aimed the determination of estrogens.

2. Experimental

2.1. Materials and chemicals

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25%, w/w), sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Sodium dodecylsulfate (SDS) was obtained from Sigma (St Louis, MO, USA). MWCNTs-OH (purity > 95 wt%, outer diameter < 8 nm and length 0.5–2 μm) was purchased from Chengdu Organic Chemistry Company (Chengdu, China). Acetonitrile and methanol (HPLC grade) were purchased from SK Chemicals (Ulsan, South Korea). Methyltrimethoxysilane (MTMOS), poly (methylhydrosiloxane) (PMHS), tetraethyl orthosilicate (TEOS), trifluoroacetic acid (TFA) were purchased from Acros Organics (Geel, Belgium). These reagents were used without any further purification.

Diethylstilbestrol, estrone, and estriol were purchased from Chem Service (West Chester, PA, USA). Stock solutions of standards were prepared as 1 mg mL^{-1} in methanol and stored at 4 °C in brown vials.

Ultra-pure water (18.2 M Ω) used for background electrolyte solution, sample preparation and for the synthesis of particles was obtained from an Elga water purification system (ELGA, London, UK).

2.2. Instrumentation

KS-250E II ultrasonic cleaner (Ningbo Haishu Kesheng Ultrasonic Equipment Company, Ningbo, China) was used for the preparation of particles. Temperature-controlling process for the aging of particles was carried out using a gas chromatography (GC) system 7890 II (Techcompany, Shanghai, China). All electrophoresis experiments were performed on a Beckman P/ACE MDQ capillary electrophoresis system (Beckman Coulter Company, Brea, CA, USA) equipped with a photodiode array UV absorption detector. Data acquisition and analysis were carried out using Beckman P/ACE system MDQ version 32 Karat software. All separations were performed in a fused-silica capillary (60.2 cm total length (50 cm effective length) \times 50 μm i.d.) (Hebei Yongnian Ruipu Chromatogram Equipment Company, Handan, China). A new capillary was conditioned prior to its first use by sequentially flushing with 1 mol L^{-1} NaOH for 30 min, water for 3 min, CH_3OH for 30 min, water for 30 min and finally with buffer (50 mmol L^{-1} SDS–50 mmol L^{-1} H_3PO_4 –20% acetonitrile (pH 2.0)) for 60 min.

After each run, the capillary was preceded by a 2 min rinse with 0.1 mol L^{-1} NaOH, 2 min rinse with H_2O followed by 3 min rinse with the background electrolyte. The background electrolyte was renewed every three runs for good reproducibility.

All solutions used in electrophoresis experiments were sonicated and filtered through 0.45 μm filters (Sartorius, Gottingen, Germany) prior to use.

2.3. Preparation of magnetic MWCNTs-OH particles

2.3.1. Preparation of magnetic silica particles

Magnetic Fe_3O_4 particles were prepared based on the chemical co-precipitation of Fe^{3+} and Fe^{2+} under a basic condition according to previously reported procedure [21]. The black magnetic Fe_3O_4 particles were then rinsed several times with water and ethanol, and dispersed in ethanol for further use.

Magnetic silica particles were prepared by sol-gel method [33] with some modifications. Magnetic Fe_3O_4 particles prepared by co-precipitation (2.0 g) were dispersed in a mixture containing 100 mL ethanol, 32 mL deionized water and 2 mL TEOS with vigorous stirring. The mixture was heated to 40 °C. Then, 2 mL of ammonium hydroxide (25%, w/w) was added to the dispersion and the reaction was allowed to proceed for 12 h. Finally, the particles were rinsed several times with methanol and dried under a vacuum at 30 °C.

2.3.2. Preparation of magnetic MWCNTs-OH particles

Taking into account the limited solubility of MWCNTs in organic solvent (ethanol, benzene, toluene, dimethylbenzene, hexane, etc.), functionalized MWCNTs (MWCNTs-OH) was used to improve the solubility of MWCNTs in organic medium [34]. First, the sol solution was prepared using the following procedure. MWCNTs-OH (2 mg) was dissolved in 400 μL of MTMOS (sol-gel precursor) and the mixture was vortexed for 30 s. Then, 50 μL of deionized water and 50 μL of PMHS (deactivation reagent) were added to the mixture followed by vortexing for 30 s. The mixture was sonicated for 30 min in ice bath. Afterwards, TFA (50 μL) was added to the mixture, and followed by sonication for 10 min. A sol solution was formed.

Magnetic silica particles were first treated with HCl aqueous solution (1 mol L^{-1}) and then dried under nitrogen atmosphere at 120 °C for 1 h. Then, the magnetic silica particles (0.05 g) were added to the prepared sol solution, followed by sonication in ice bath for 30 min. Afterwards, the mixture was placed at room temperature for 24 h and conditioned under nitrogen atmosphere in a GC oven by programming the temperature from 40 to 260 °C at 2 °C/min and held at the final temperature for 4 h. Finally, the prepared magnetic MWCNTs-OH particles were ground and sieved to sizes lesser than 5 μm . The final product was washed with methanol and deionized water, and dried for use.

2.4. Characterization

Raman spectra of the magnetic MWCNTs-OH particles were obtained with a triple grating spectrometer (Acton Spectro@2300 i, Princeton Acton, USA). The spectral resolution was set at 4 cm^{-1} . The detector was a charge-coupled device cooled by liquid nitrogen. The 514.5 nm line of an argon ion laser was used as the excitation source for Raman measurements. The laser power at the samples was 10 MW.

2.5. Procedure of magnetic extraction

The tap water used for this study was taken from our lab. The mineral water and honey were purchased from a local market, and the river water was collected from the Pearl River (Guangzhou,

China). Analytes were extracted directly from the mineral water and tap water samples using magnetic MWCNTs–OH particles. The river water was first centrifuged at 25 °C and 5000 rpm for 30 min to remove solid particles. Then, the analytes were extracted from the supernatant using the MWCNT–functionalized magnetic particles. The honey sample (1 g) was dissolved in 10 mL ultra-pure water. The analytes were extracted from the diluted honey sample solution using the MWCNT–functionalized magnetic particles, followed by sweeping MEKC analysis.

Magnetic MWCNTs–OH particles (0.1 g) were first activated with methanol and water separately in sequence. Then the particles were added to the water sample (10 mL). The mixture was sonicated at room temperature for 3 min. Then, the magnetic MWCNTs–OH particles were separated rapidly from the solution using a magnetic separator (Dynal MPC-L, Invitrogen Corporation, Carlsbad, CA, USA). After discarding the supernatant, estrogens were eluted from the magnetic MWCNTs–OH particles with 2 mL of methanol under sonication for 5 min. The eluent was evaporated to dryness using a micro-centrifugal vacuum concentrator (Christ RVC 2-18, Osterode am Harz, Germany) at 30 °C. Prior to analysis the dried extracts were reconstituted in 1.0 mL of 50 mmol L⁻¹ phosphoric acid.

2.6. Sweeping MEKC

Sweeping MEKC analysis of estrogens was performed according to a procedure previously reported [21]. Briefly, the background electrolyte for MEKC consisted of 50 mmol L⁻¹ SDS–50 mmol L⁻¹ H₃PO₄–20% acetonitrile (pH 2.0) (6.2 mS cm⁻¹). The capillary temperature was set at 20 °C and the separation voltage was –25 kV. Absorption photometric measurements were made at 196 nm. The sample solutions in 50 mmol L⁻¹ H₃PO₄ (5.9 mS cm⁻¹) were injected into the capillary under a pressure of 0.138 MPa for 15 s. The stock solutions were diluted to the required concentration with 50 mmol L⁻¹ H₃PO₄ prior to separation. Sweeping was used as an on-line sample concentration method to enhance the detectability of estrogens.

3. Results and discussion

3.1. Characterization of magnetic MWCNTs–OH particles

Raman spectroscopy was employed to analyze the magnetic silica particles, MWCNTs–OH and the magnetic MWCNTs–OH particles. Fig. 1 shows the Raman spectra of these particles. There were two characteristic peaks at ~1357 cm⁻¹ (D line) and ~1593 cm⁻¹ (G line) in the Raman spectra of MWCNTs–OH, which resulted from its own structural defects. In the Raman spectra of magnetic MWCNTs–OH particles, two peaks at ~1354 cm⁻¹ and ~1590 cm⁻¹ were also observed, which demonstrated that the MWCNTs–OH were successfully modified on the surface of magnetic silica particles by sol–gel technology through the reaction of MWCNTs–OH, MTMOS and –OH on the surface of silica particles. In the sol–gel process, MWCNTs–OH and MTMOS generated a sol–gel network, which were covalently bonded to the surface of the magnetic silica particles. The characteristic peaks of magnetic silica particles also appeared in the spectra of magnetic MWCNTs–OH particles.

3.2. Optimization of magnetic extraction conditions

Estrogens were used as model compounds to evaluate the performance of the prepared magnetic MWCNTs–OH particles for the extraction of hydrophobic compounds. A mixture of three estrogens (the concentration of each analyte was 0.2 µg mL⁻¹) was used

Table 1
Optimized extraction conditions for estrogens.

Factor	Condition
Adsorbent	Magnetic MWCNTs–OH particles (0.1 g)
Activation procedure	Methanol and water separately in sequence
Desorption solvent	Methanol (2 mL)
Extraction time	3 min
Desorption time	5 min
Supplementary condition	Sonication

for the optimization of magnetic extraction conditions. Several factors affecting the extraction efficiency were investigated using 0.1 g of magnetic MWCNTs–OH particles as adsorbents.

Sonication was utilized to accelerate the adsorption of estrogens on the magnetic MWCNTs–OH particles and desorption from the particles. Before the extraction experiments, the magnetic particles were activated with methanol and water. First, the influence of the extraction time on the extraction efficiency was studied. When the extraction time was less than 3 min, the extraction efficiencies of the estrogens increased with the increase of the extraction time (Fig. 2). Further increasing the extraction time, the extraction efficiencies slowly decreased. With the extraction time at 3 min, the extraction efficiencies for the three estrogens were the largest ones.

When dried magnetic particles were directly used for the extraction of estrogens in water without the activation using methanol and water, the extraction efficiencies for the estrogens were lower than those using the previously activated particles. The results demonstrated that the activation process for the magnetic particles was important. Then, methanol was used as the desorption solvent. The effect of the volume of the desorption solvent (methanol) and desorption time were investigated to ensure the adsorbed analytes being completely desorbed from the particles. The experimental results indicated that 2 mL of methanol was enough to desorb the analytes adsorbed on the magnetic MWCNTs–OH particles. When desorption time was 5 min, the extraction efficiencies for the estrogens were the largest (Fig. 3). Further prolonging desorption time was unfavorable. No carryover was found after the magnetic MWCNTs–OH particles were desorbed in methanol (2 mL) for 5 min. Therefore, the MWCNT–OH particles can be re-utilized.

Under the optimized conditions (Table 1), the extraction efficiencies of diethylstilbestrol, estrone, and estriol were 95.8%, 94.1%, and 52.3%, respectively. The fast extraction and desorption process demonstrated that sonication was beneficial to accelerate the distribution equilibrium of the analytes between the magnetic particles and the sample solution.

3.3. Adsorption capacity

The adsorption capacity of the magnetic MWCNTs–OH particles was investigated. Diethylstilbestrol was used for the study of the adsorption capacity of the particles since its extraction efficiency was the largest. The magnetic particles were used as the adsorbents and the extraction experiments were carried out in different concentrations of diethylstilbestrol. The adsorption amount of the magnetic particles reached the maximum when the concentration of diethylstilbestrol was 60 µg mL⁻¹. Further increasing the concentration of diethylstilbestrol, the adsorption amount almost remained constant. The adsorption capacity of the prepared particles was calculated to be 5.23 mg/g according to the average extraction efficiency of diethylstilbestrol (95.9%).

3.4. Method validation

Sweeping MEKC method was used for the determination of the estrogens. The current methods for the determination of estrogens

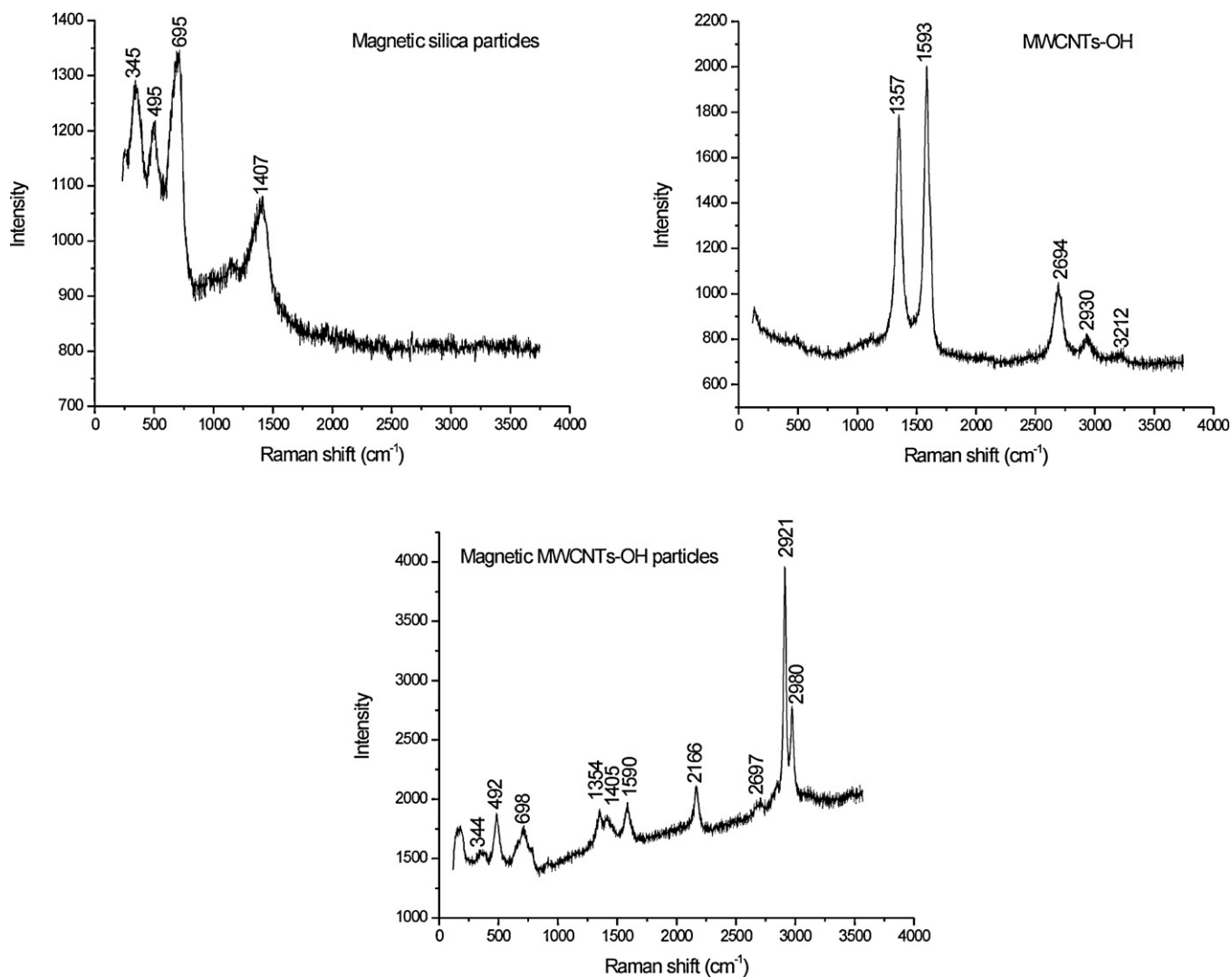


Fig. 1. Raman spectra of magnetic silica particles, MWCNTs-OH and magnetic MWCNTs-OH particles.

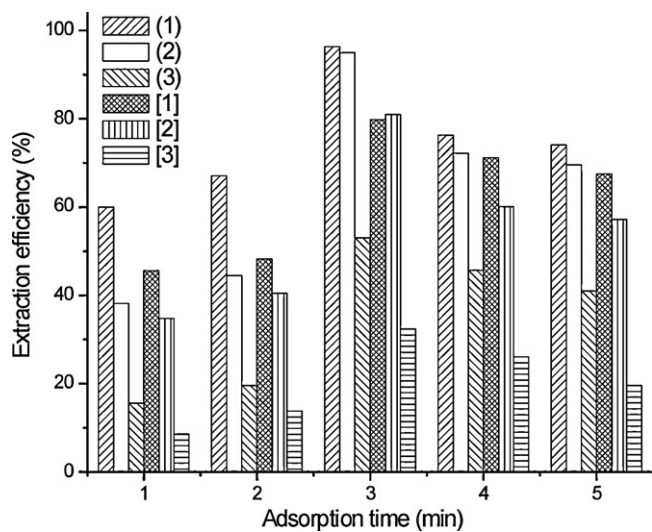


Fig. 2. Effect of adsorption time on the extraction efficiency of estrogens. Experimental conditions: desorption time, 5 min; elute solvents, 2 mL methanol; the concentration of each analyte was $0.2 \mu\text{g mL}^{-1}$. 1, diethylstilbestrol; 2, estrone; 3, estriol; (), activated magnetic MWCNTs-OH particles with methanol and water separately in sequence; [], dried magnetic MWCNTs-OH particles.

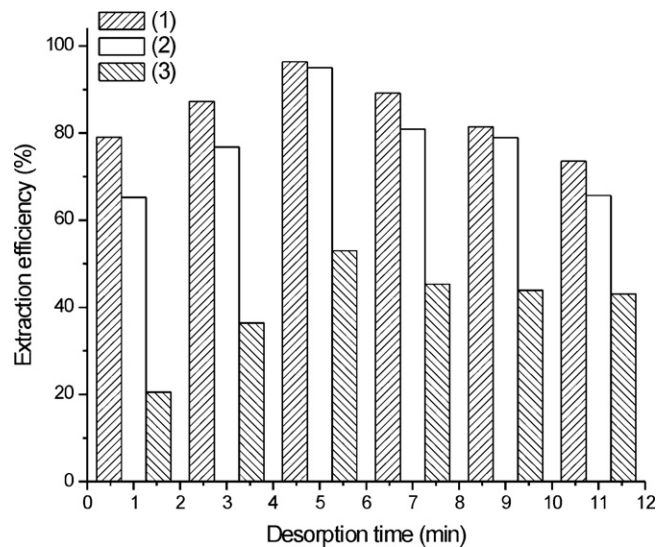


Fig. 3. Effect of desorption time on the extraction efficiency of estrogens. Experimental conditions: adsorption time, 3 min; elute solvents, 2 mL methanol; the concentration of each analyte was $0.2 \mu\text{g mL}^{-1}$. 1, diethylstilbestrol; 2, estrone; 3, estriol.

Table 2
Reproducibility, linearity and sensitivity for three estrogens by sweeping MEKC.

Analyte	Calibration line	<i>r</i>	LOD ^a (ng mL ⁻¹)	LOQ ^b (ng mL ⁻¹)	RSD (% , <i>n</i> = 3)	
					Migration time	Peak area
Diethylstilbestrol	$y = 59.9x + 2.2$	0.9994	0.9	2.9	1.7	2.5
Estrone	$y = 40.8x - 2.2$	0.9985	1.7	5.7	1.9	1.4
Estriol	$y = 73.7x + 0.01$	0.9995	1.0	3.5	1.0	1.2

y: peak area; *x*: analyte concentration (μg mL⁻¹); *r*: correlation coefficient.

^a S/N=3.

^b S/N=10.

are mainly based on GC [35,36], high performance liquid chromatography (HPLC) [37,38], and MEKC [39,40]. In GC, estrogens have to be derivatized since non-volatile chemicals cannot be analyzed directly by GC. HPLC is the most employed technique for the determination of estrogens. However, with MEKC, good separation and detection are also achieved with less demand for organic solvents and, therefore, producing less waste.

Figures of merit of the sweeping MEKC method were obtained. In Table 2, it is indicated the reproducibility data obtained for the retention time and peak height, the calibration function (peak area versus concentration in μg mL⁻¹), linear response of the calibration curve, limit of detection (LOD) and limit of quantification (LOQ) for the determination of the three estrogens. The LOD was calculated based on signal-to-noise ratio of 3 (S/N=3). The LOQ was determined at signal-to-noise ratio equal to 10 (S/N=10). The calibration curves exhibited linear behavior with correlation coefficient above 0.9985 in the range 0.1–10 μg mL⁻¹. The repeatability was calculated by triplicate analysis of standard sample (the concentration of each of the analytes was 1 μg mL⁻¹). The relative standard deviations (RSDs) for the migration times and peak areas of the analytes were less than 2.5%. In comparison with the HPLC methods, the sweeping MEKC method offered similar detection sensitivities for the estrogens.

The extraction efficiencies of the MWCNT–OH particles were studied using different concentration levels of estrogens under the optimum extraction conditions. As shown in Table 3, the extraction efficiencies ranged from 52.4% to 95.9% with RSDs lower than 3.6% based on triplicate measurements at each level. The average extraction efficiencies for diethylstilbestrol, estrone and estriol in the concentration range 0.01–1 μg mL⁻¹ were 95.9%, 93.9%, and 52.4%, respectively. log *P* (octanol–water partition coefficient) value reflects hydrophobicity of diethylstilbestrol (5.07), estrone (3.13) and estriol (2.45) [41]. The experimental results showed that the extraction efficiency of the analytes decreased with the decrease of their log *P* (octanol–water) value. Compared to a previously published work [21] which aimed the determination of estrogens, the extraction efficiencies for diethylstilbestrol and estrone using magnetic MWCNTs–OH particles as adsorbents were significantly improved. In comparison with previously published traditional SPE methods using C-18 cartridges [10,11], the extraction efficiency of diethylstilbestrol using the proposed method was superior to that of SPE methods, while the extraction efficiencies of

Table 3
Extraction efficiencies at different levels of estrogens (*n* = 3).

Analyte	Diethylstilbestrol	Estrone	Estriol
0.01 μg mL ⁻¹			
Extraction efficiency (%)	97.1	95.2	50.2
RSD (%)	0.5	1.4	1.5
0.05 μg mL ⁻¹			
Extraction efficiency (%)	95.7	93.6	52.3
RSD (%)	3.0	3.1	1.4
0.1 μg mL ⁻¹			
Extraction efficiency (%)	95.8	93.5	51.5
RSD (%)	3.6	1.2	2.0
0.5 μg mL ⁻¹			
Extraction efficiency (%)	96.0	93.1	53.6
RSD (%)	1.0	1.6	1.4
1 μg mL ⁻¹			
Extraction efficiency (%)	94.8	94.2	54.2
RSD (%)	1.3	1.7	1.6
Average extraction efficiency (%)	95.9	93.9	52.4

estrone and estriol were inferior to those of SPE methods. The primary advantage of the MSPE method is that the adsorbents need not be packed into the SPE cartridges and the phase separation can be conveniently realized by applying an external magnetic field. The MSPE procedure is simpler.

Figures of merit using the extraction and pre-concentration of estrogens in the MWCNT–OH particles are indicated in Table 4. The precision was determined by analyzing the samples with the concentration of each of the analytes at 0.1 μg mL⁻¹ based on triplicate experiments. The LODs of the three estrogens were less than 0.2 ng mL⁻¹ (S/N=3). The calibration coefficients of the calibration curves for the estrogens were above 0.9977. The RSDs for the migration time and peak area of each estrogen were less than 3.9%.

3.5. Application to real samples

The proposed magnetic extraction–sweeping MEKC method was used to determine the content of the three estrogens in tap water, mineral water, the Pearl River water and honey. The estrogens in the samples were not detected. The analyte fortified samples were analyzed. Fig. 4 illustrates the electropherograms of the standards mixture, the blank and the analyte fortified samples after extraction using the magnetic MWCNTs–OH particles. Peaks of the

Table 4
Reproducibility, linearity and sensitivity for three estrogens by coupling extraction using the magnetic MWCNTs–OH particles and sweeping MEKC.

Analyte	Calibration line	<i>r</i>	LOD ^a (ng mL ⁻¹)	LOQ ^b (ng mL ⁻¹)	RSD (% , <i>n</i> = 3)	
					Migration time	Peak area
Diethylstilbestrol	$y = 550.2x + 5.0$	0.9993	0.1	0.3	0.5	3.9
Estrone	$y = 381.0x - 5.2$	0.9977	0.2	0.5	0.9	1.2
Estriol	$y = 385.7x + 1.7$	0.9988	0.2	0.6	1.2	0.3

y: peak area; *x*: analyte concentration (μg mL⁻¹); *r*: correlation coefficient.

^a S/N=3.

^b S/N=10.

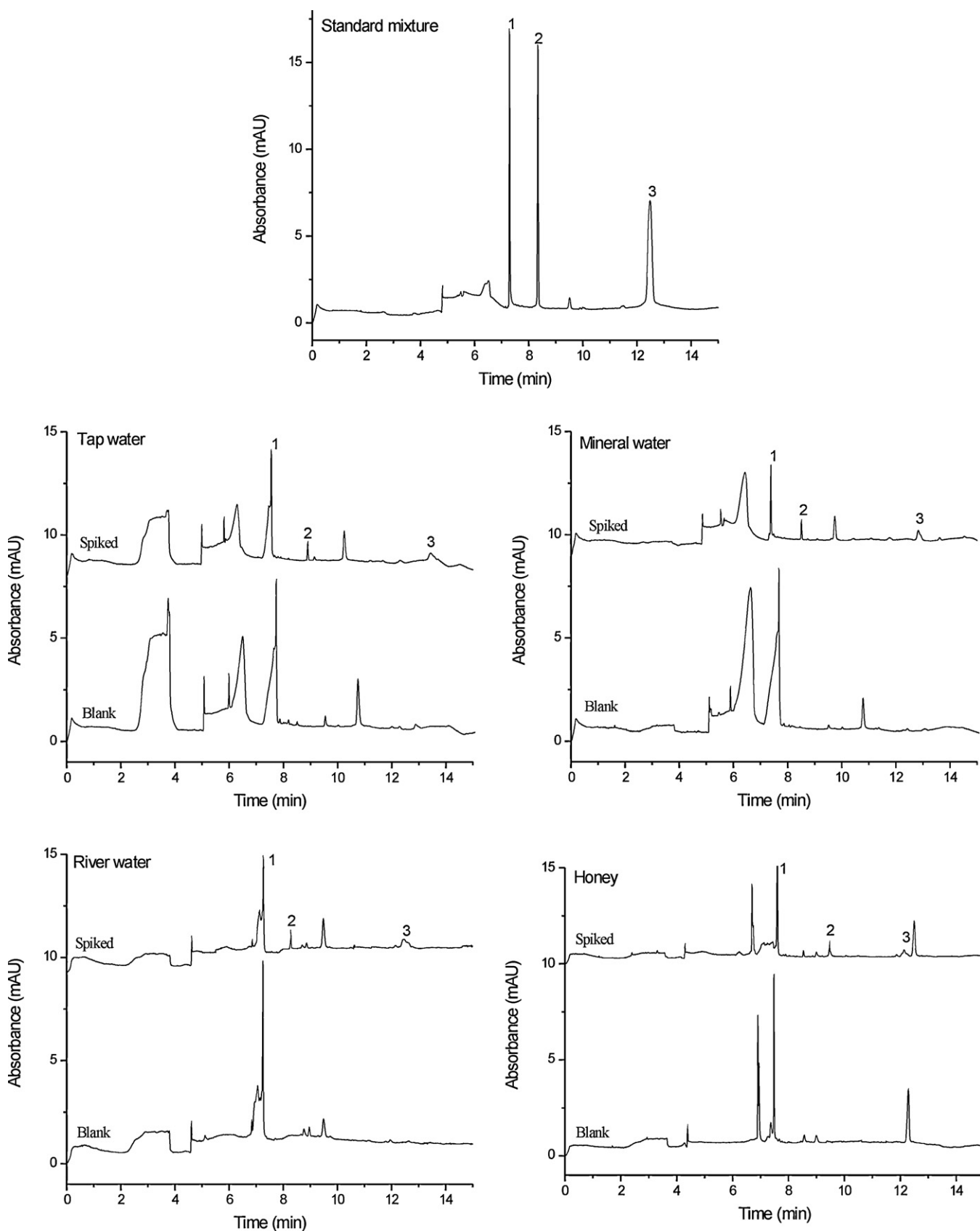


Fig. 4. Electropherograms of standards mixture and water samples using sweeping MEKC after extraction using magnetic MWCNTs–OH particles. Experimental conditions: fused-silica capillary 60.2 cm (effective length 50 cm) \times 50 μ m i.d.; buffer, 50 mmol L⁻¹ SDS–50 mmol L⁻¹ H₃PO₄–20% acetonitrile (pH 2.0); applied voltage, –25 kV; hydrodynamic injection, 0.138 MPa \times 15 s; capillary temperature, 20 °C; detection wavelength, 196 nm; samples solvent, 50 mmol L⁻¹ phosphoric acid. Analytes: 1, diethylstilbestrol; 2, estrone; 3, estriol.

Table 5
Analysis results of tap water, mineral water, the Pearl River water and honey sample.

Sample	Analyte	RSD (% , n=3)		C ($\mu\text{g mL}^{-1}$)		Recovery (%)
		Migration time	Peak area	Added value	Found value ^a	
Tap water	Estrone	1.2	2.5	0.01	0.0090	96.2 ± 2.3
	Estriol	1.5	1.0	0.01	0.0052	99.8 ± 1.2
Mineral water	Estrone	1.1	3.2	0.01	0.0093	98.7 ± 3.5
	Estriol	1.6	2.5	0.01	0.0052	99.3 ± 1.3
River water	Estrone	0.2	1.6	0.01	0.0092	97.7 ± 1.6
	Estriol	0.4	1.5	0.01	0.0051	98.3 ± 1.4
Honey	Estrone	0.9	2.6	0.01	0.0086	91.2 ± 2.0
	Estriol	1.5	1.9	0.01	0.0047	89.5 ± 1.9

^a Found value: concentration taking the extraction efficiency into account.

analytes monitored in the analyte fortified samples were identified by their migration times in comparison with external standards and by standard addition method. The recoveries of the estrogens in the analyte fortified samples were determined based on the average extraction efficiency and the analyte amount added to the real sample (concentration of each analyte $0.01 \mu\text{g mL}^{-1}$) by triplicate analysis. Since the sample matrix seriously interfered with the quantification of diethylstilbestrol, its recovery was not determined. The recoveries of two estrogens in the analyte fortified samples were shown in Table 5. The satisfactory recoveries and RSDs demonstrate that the magnetic MWCNTs–OH particles are one kind of potential materials for the extraction of organic pollutants in environmental water.

4. Conclusions

In this work, magnetic MWCNTs–OH particles were successfully synthesized by sol–gel technology for the first time. In the sol–gel process, MWCNTs–OH and MTMOS generated a sol–gel network, which were covalently bonded to the surface of the magnetic silica particles. The magnetic MWCNTs–OH particles were applied for the extraction of low concentrations of estrogens from water and honey samples, followed by sweeping MEKC analysis. Sonication was utilized to accelerate the adsorption of estrogens on the MWCNTs–OH particles and desorption from the particles. The extraction efficiencies for diethylstilbestrol, estrone and estriol were 95.9%, 93.9%, and 52.4%, respectively. Compared to a previously published work [21] which aimed the determination of estrogens, the extraction efficiencies for diethylstilbestrol and estrone using MWCNTs–OH particles as adsorbents were significantly improved. The work extended the application of magnetic SPE technology in environmental samples.

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