Separation and Purification Technology 182 (2017) 78–86

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Sensitive determination of bisphenol A, 4-nonylphenol and 4-octylphenol by magnetic solid phase extraction with Fe@MgAl-LDH magnetic nanoparticles from environmental water samples

Qingxiang Zhou *, Man Lei, Jing Li, Kuifu Zhao, Yongli Liu

College of Geosciences, China University of Petroleum Beijing, Beijing 102249, China

ARTICLE INFO

Article history:
Received 17 June 2016
Received in revised form 21 October 2016
Accepted 15 January 2017
Available online 24 March 2017

Keywords:
Bisphenol A
4-Octylphenol
4-Nonylphenol
Fe@MgAl-LDH
Magnetic solid phase extraction

ABSTRACT

Mg-Al-layered double hydroxide (Mg-Al-LDH) modified nanoscale zero-valent iron (NZVI) (Fe@MgAl-LDH) was firstly synthesized and characterized by several techniques. The results showed that the layered double hydroxides were coated on the surface of nanoscale zero-valent iron particles. This new material exhibited good adsorption for bisphenol A, 4-octylphenol and 4-nonylphenol from water samples. Based on these, a sensitive method was developed for the extraction and preconcentration of bisphenol A, 4-octylphenol and 4-nonylphenol using magnetic Fe@MgAl-LDH nanoparticles as the solid phase extraction adsorbents prior to high performance liquid chromatography coupled with variable wavelength detection. Under the optimal conditions, linear responses were achieved in the range of 0.5–200 μg L^{-1} with the correlation coefficients (r) above 0.999. The detection limits of three analytes were in the range of 0.24–0.34 μg L^{-1}, and precisions were all below 2.5% (n = 6). The proposed method was evaluated with real water samples and the excellent spiked recoveries in the range of 96.0–99.3% were achieved.

1. Introduction

Bisphenol A, 4-octylphenol and 4-nonylphenol are well known endocrine disrupting chemicals. Because of impacting the structure or function of the endocrine system, they have absorbed a lot of attention over the past decades [1,2]. Bisphenol A is a raw material widespread used in the synthesis of polycarbonate, epoxy resin, thermal paper, polysulfone resin, polyphenylene ether resin, unsaturated polyester resins and other polymer materials, which are extensively used to produce polycarbonate water bottles, milk packaging, baby water bottles, plastic food containers, beverage cans, water supply pipes, toys, cigarette filters, kitchen utensils and even medical equipments, including medical tubing and implant devices [3–5]. Moreover, bisphenol A can cause adverse health effects on animals and humans because of its endocrine disruption activity, oxidative and mutagenic potential as well as hypomethylation ability, thereby leading to obesity, diabetes, miscarriages and cardiovascular disease, interfering with the human endocrine system, lowering the immune function and increasing the cancer risk of the mammary gland and prostate [4,6]. In Chinese standard for drinking water, bisphenol A concentration was limited to be lower than 0.01 mg L^{-1} [7]. 4-octylphenol and 4-nonylphenol can also perturb reproductive and immune function with adverse effects on health [8,9], and US EPA has accepted the risks of nonylphenol and has prepared a guideline for ambient water quality that recommends nonylphenol concentration in freshwater be below 6.6 μg L^{-1} [10]. Consequently, it is urgent to propose efficient and sensitive determination methods to monitor bisphenol A, 4-octylphenol and 4-nonylphenol in water samples.

To date, various methods have been developed for determination of bisphenol A, 4-octylphenol and 4-nonylphenol including liquid chromatography [11], liquid chromatography-mass spectrometry [12,13], gas chromatography-mass spectrometry [14,15], and electrochemical sensors [16]. However, complex sample matrices and insufficient sensitivity of some analytical instruments make difficult directly determine pollutants at low concentrations in the environment. Therefore, a pretreatment or pre-concentration step is required before analysis. Many sample pretreatment techniques have been developed which included liquid phase microextraction [17,18], solid phase extraction [19,20], ion exchange [21,22], solvent extraction [23,24] and so on. Among these methods, solid phase extraction (SPE) is commonly and widely used for sample pretreatment due to its simplicity, flexibility, rapidness, high recoveries, good enrichment factors and low consumption of organic solvents [25,26]. However, SPE still has

* Corresponding author.
E-mail address: zhouqx@cup.edu.cn (Q. Zhou).

http://dx.doi.org/10.1016/j.seppur.2017.01.071
1383-5866/

drawbacks as it is performed in a column and the contact area between the adsorbents and analytes is limited. Recently, magnetic solid phase extraction (MSPE), a new mode of SPE, has been developed using magnetic nanoparticles as the adsorbent due to its high extraction efficiency, simple separation procedure, low cost and good reusability [27–29]. In magnetic solid phase extraction procedure, the adsorbents are dispersed into the solution and the contact area between the adsorbents and analytes is much larger. Moreover, the adsorbents can be simply isolated from the solution with an external magnet, which makes separation much easier and faster.

Nanoscale zero-valent iron, as an effective nanomaterial, has been widely used in groundwater, soil and hazardous waste treatment [30,31]. Compared to larger iron particles, nanoscale zero-valent iron (NZVI) takes advantage of higher reactivity, faster reaction, higher reduction and sorption capabilities due to its larger specific surface and more reactive sites on the surface [32–34]. However, there are very few reports on its application for trace enrichment of pollutants due to its bad stability, easy oxidation and easy aggregation. However it is very easy to resolve this problem by modifying with a layer coating. In order to increase the extraction efficiency and adsorption capacity of magnetic nanoparticles, the surfaces can be modified with reasonable material containing special functional groups.

Layered double hydroxides (LDHs), commonly referred to as hydrotalcite-like materials and anionic clays, have received much attention in recent years. Their structure consists of positively charged stacked brucite-like octahedral hydroxide layers due to the isomorphous replacement of some divalent metal cation by trivalent metal cation, and anions must intercalate between adjacent layers in order to maintain charge neutrality [35,36]. Layered double hydroxides are widely used as catalysts, sorbents, ion-exchangers and antacids due to the layered structure, high anionic exchange capability, large surface area, high porosity and thermal stability, good dispersion of the cations in the layered sheets and easy to insert catalytic active sites [37,38]. The general formula for layered double hydroxides (LDHs) can be expressed as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O$, where M^{2+} is a divalent cation (Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+} or Fe^{2+}), M^{3+} is a trivalent cation (Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}), and A^{n-} is an interlayer anion(Cl^-, NO_3^-, ClO_4^-, CO_3^{2-}, SO_4^{2-}), which can be almost any organic or inorganic anion, and x is the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$, ranging from 0.2 to 0.33 for pure LDH formation [39–41]. At present, layered double hydroxides are synthesized by various methods, such as coprecipitation at constant pH, sol-gel, and urea hydrolysis. Among the various synthetic routes, coprecipitation at constant pH is the best one for use. As reported in previous studies, there have been many studies focusing on the application of layered double hydroxides as adsorbents using different interlayer anions. You et al. developed a coprecipitation method for synthesizing magnesium aluminum layered double hydroxide (Mg-Al LDH) and organo-LDHs were prepared by equilibrating the synthesized Mg-Al LDH in different anionic surfactant solutions [41]. Chen et al. described a rapid coprecipitation method under ambient condition to synthesize center-hollowed magnetic core-shell hierarchical submicrospheres Fe_3O_4@CuNiAl-LDH [42]. Legrouri et al. prepared Zn-Al-Cl layered double hydroxides for the removal of the herbicide 2,4-dichlorophenoxyacetate from contaminated aqueous solutions [43].

In this study, a novel magnetic nanomaterial Fe@MgAl-LDH was firstly prepared with nanoscale zero-valent iron as the core and MgAl-LDH as the shell, and which was used as the adsorbent for magnetic solid phase extraction prior to high performance liquid chromatography coupled with variable wavelength detection (HPLC-UV) for the determination of bisphenol A, 4-octylphenol and 4-nonylphenol in environmental water samples. Fe@MgAl-LDH magnetic materials were synthesized by a two-step method and then characterized by transmission electron microscopy (TEM). The experimental parameters including eluent, solution pH, adsorbent amount, adsorption time, elution time,

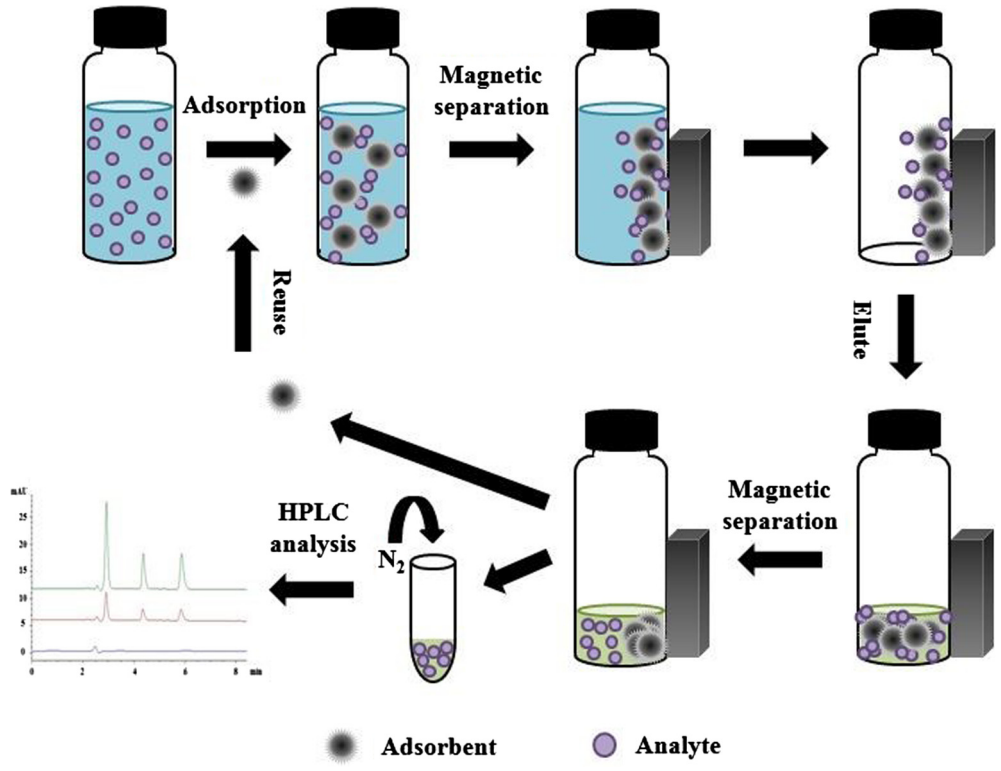

Fig. 1. Typical extraction and magnetic separation procedure.

eluent volume, ionic strength, humic acid and sample solution were optimized.

2. Experimental

2.1. Chemicals and materials

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) was obtained from Sinopharm Chemical Reagent Co. Ltd. Sodium hydroxide, hydrochloric acid (37%), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) and aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) were obtained from Beijing Chemical Works (Beijing, China). Hydrazine hydrate ($N_2H_4{\cdot}H_2O$), bisphenol A (BPA), 4-octylphethol (4-OP), 4-nonylphethol (4-NP), ethanol, methanol, acetonitrile, acetone and ethyl acetate were obtained from Aladdin Chemistry Co. Ltd. An Agilent 1260 HPLC system with an ultraviolet variable wavelength detector (VWD) (Santa Clara, USA) was used for the analysis. An InertSustain C18 column (4.6 × 250 mm, 5 μm) was used for separation. The ultrapure water was used in all experiments.

2.2. Preparation of Fe@MgAl-LDH

The Fe nanocubes were synthesized according to a previous report [44]. In the preparation procedure, 2.4 g $FeCl_3{\cdot}6H_2O$ was dissolved in 12 mL ethanol. Under magnetic stirring, 3.0 g NaOH and 6 mL $N_2H_4{\cdot}H_2O$ (80 wt%) were added. Then, the mixture was sealed in a 50 mL autoclave and heated at 80 °C for 10 h. After cooled to ambient temperature, the black powders were collected and washed with deionized water and ethanol for several times, and vacuum dried at 50 °C.

The Fe@MgAl-LDH magnetic nanoparticles were prepared by coprecipitation method. The prepared Fe (300 mg) was ultrasonically dispersed into 45 mL ethanol (70%) in 250 mL beaker for

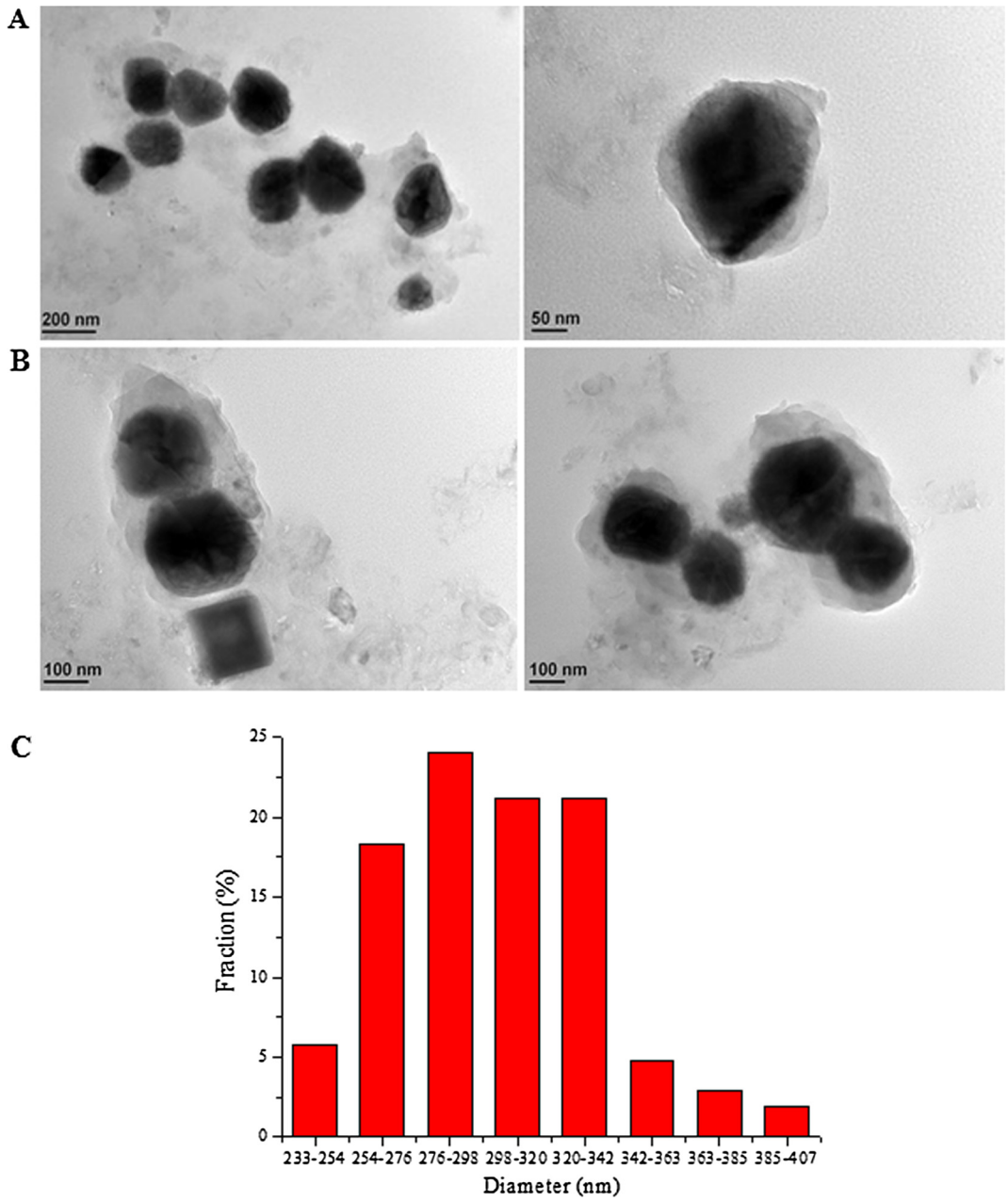

Fig. 2. TEM images of (A) Fe@MgAl-LDH particles; (B) Fe@MgAl-LDH particles after use; (C) particle size distribution.

20 min, then put into 20 °C water bath with vigorous stirring. A salt solution containing 0.96 g $Mg(NO_3)_2{\cdot}6H_2O$ and 0.46 g $Al(NO_3)_3{\cdot}9H_2O$ was added drop wisely into the suspension, NaOH solution was added simultaneously to keep the pH at about 11. Then, the solution was aged for 1 h, further washed with deionized water for several times and finally vacuum dried at 50 °C overnight.

2.3. SPE procedure

First, 50 mg Fe@MgAl-LDH adsorbents were dispersed into 60 mL filtered water samples containing target compounds at trace level. The suspension was stirred for 40 min to facilitate the adsorption of BPA, 4-OP, 4-NP on the surface of Fe@MgAl-LDH adsorbents. Subsequently, a magnet was put under the bottom of the beaker and the supernatant was completely decanted. Then the analytes were desorbed from the particles by adding 4 mL acetone for four times (90 s each time). After desorption, the eluent was separated by magnet and evaporated to dryness under nitrogen gas flow. The dried residue was dissolved in 200 μL methanol for HPLC analysis. The typical extraction and magnetic separation procedure was demonstrated in Fig. 1.

2.4. HPLC analysis

Bisphenol A, 4-octylphenol and 4-nonylphenol were separated and analyzed with an Agilent 1260 HPLC system. Gradient elution was carried out using water and methanol, respectively. The binary mobile phase was composed of methanol and water (95:5, v/v). The flow rate was 1 mL min^{-1} and the VWD wavelength was set at 278 nm. The injection volume was 20 μL.

3. Results and discussion

3.1. Characterization of Fe@MgAl-LDH NPs

TEM images of Fe@MgAl-LDH particles were shown in Fig. 2A. It is observed that dark Fe particles are approximately 200 nm in diameter. The prepared Fe nanoparticles are nanocubes with uniform particle size and high purity. With the added layer of LDH on the surface, the Fe@MgAl-LDH particles are rougher than that of Fe nanoparticles and have a diameter of approximate 300 nm. The Fe nanocubes are randomly coated by the gray LDH sheets. The TEM images of Fe@MgAl-LDH magnetic particles after using were shown in Fig. 2B. It can observed that the magnetic particles had no change after using, which indicated that the coating layer was stable in water. The particle size distribution of the synthesized Fe@MgAl-LDH was shown in Fig. 2C, and the average diameter of nanoparticles was approximately 302 nm. Fig. 3 shows the XRD patterns of the three kinds of materials including Fe, LDH and Fe@MgAl-LDH. For the nanoscale zero-valent iron (NZVI), which could be well indexed as the body-centered cubic phase iron, there were three remarkable diffractions at 2θ to (110), (200) and (211) planes [33]. No peaks referred to iron oxides or hydroxides are detected, indicating that pure Fe nanoparticles are synthesized in the first step. For the MgAl LDH, the different peaks at about 2θ = 11°, 23°, 35° and 61° correspond to the (003), (006), (012), (015), (113) planes, which are similar to that Wang et al. reported [35]. The intensities of the characteristic reflections for both Fe nanoparticles and MgAl-LDH in Fe@MgAl-LDH are not obviously changed compared to those in pure Fe and MgAl-LDH. In addition, no other characteristic peaks are detected, so it is believed that the synthesized Fe@MgAl-LDH is a composite of MgAl-LDH and Fe nanoparticles.

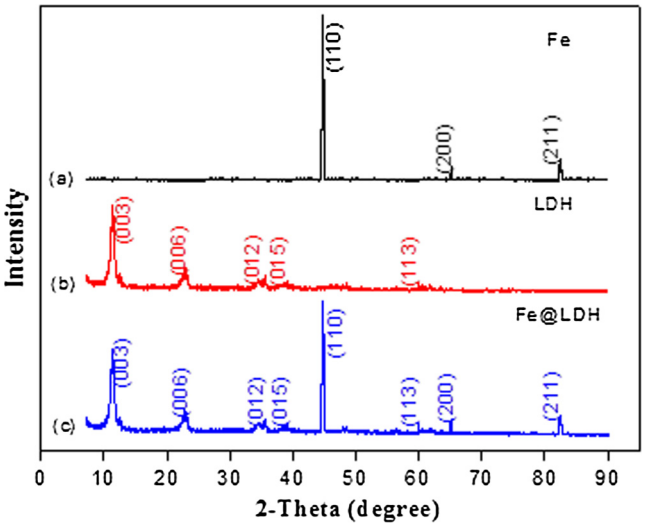

Fig. 3. XRD patterns of (A) Fe, (B) LDH and (C) Fe@MgAl-LDH.

3.2. Optimization of MSPE conditions

In the MSPE procedure, the organic solvent used as the eluent is one of the most important factors. The proper desorption solvent can effectively elute the analytes from the adsorbent and lead to a higher recovery. Hence, ethanol, methanol, acetonitrile, acetone and ethyl acetate were investigated in this experiment. As shown in Fig. 4A, it was found that the desorption ability of acetone was better than other solvents, and the other solvents resulted in similar desorption performance for the target analytes. These results indicated that acetone was an efficient eluent for these three analytes.

Generally, an appropriate pH is a crucial factor which influences adsorption efficiency. The effect of pH on the recoveries of BPA, 4-OP, 4-NP was studied in the range of pH 3–11 by adjusting with HCl and NaOH solutions and the results were shown in Fig. 4B. It can be observed that recoveries of the analytes reached the highest at pH 7, and then decreased with the increase of the pH value. When the pH value was lower than pH 7, the solution was acidic, which made hydroxide precipitates dissolve so that the structure of LDH was damaged which would decrease the adsorption active sites of Fe@MgAl-LDH. As the sample pH was near to pH 7, the three phenols existed as anions and the surface of Fe@MgAl-LDH was positive, so positively charged Fe@MgAl-LDH had efficient adsorption of the target phenols, which attributed to the strong electrostatic interactions. Meanwhile, small part of anion exchange also occurred. As the pH value increased, the analytes were inclined to ionize and the surface of Fe@MgAl-LDH was negative, which would inhibit the adsorption of the target phenols. Thus, pH 7.0 was selected for the experiments.

The absorbent amount is always a key parameter in MSPE procedure, which determines the enrichment performance good or not. In present study, it was paid more attention and investigated in the range of 30–70 mg. It can be found that when the amount of Fe@MgAl-LDH was increased from 30 to 50 mg, the recoveries of all the analytes increased quickly and then remained constant beyond 50 mg (see Fig. 4C). The recovery of BPA increased from 86% to near 100% and the recoveries of the other two phenols also increased from 70% to over 90%. These indicated that 50 mg adsorbent resulted in good adsorption of BPA, 4-OP and 4-NP. Hence, 50 mg Fe@MgAl-LDH magnetic nanoparticles were used in the following experiments.

In the MSPE procedure, sufficient contact time is crucial for the analytes to attain adsorption equilibrium on the surface of the

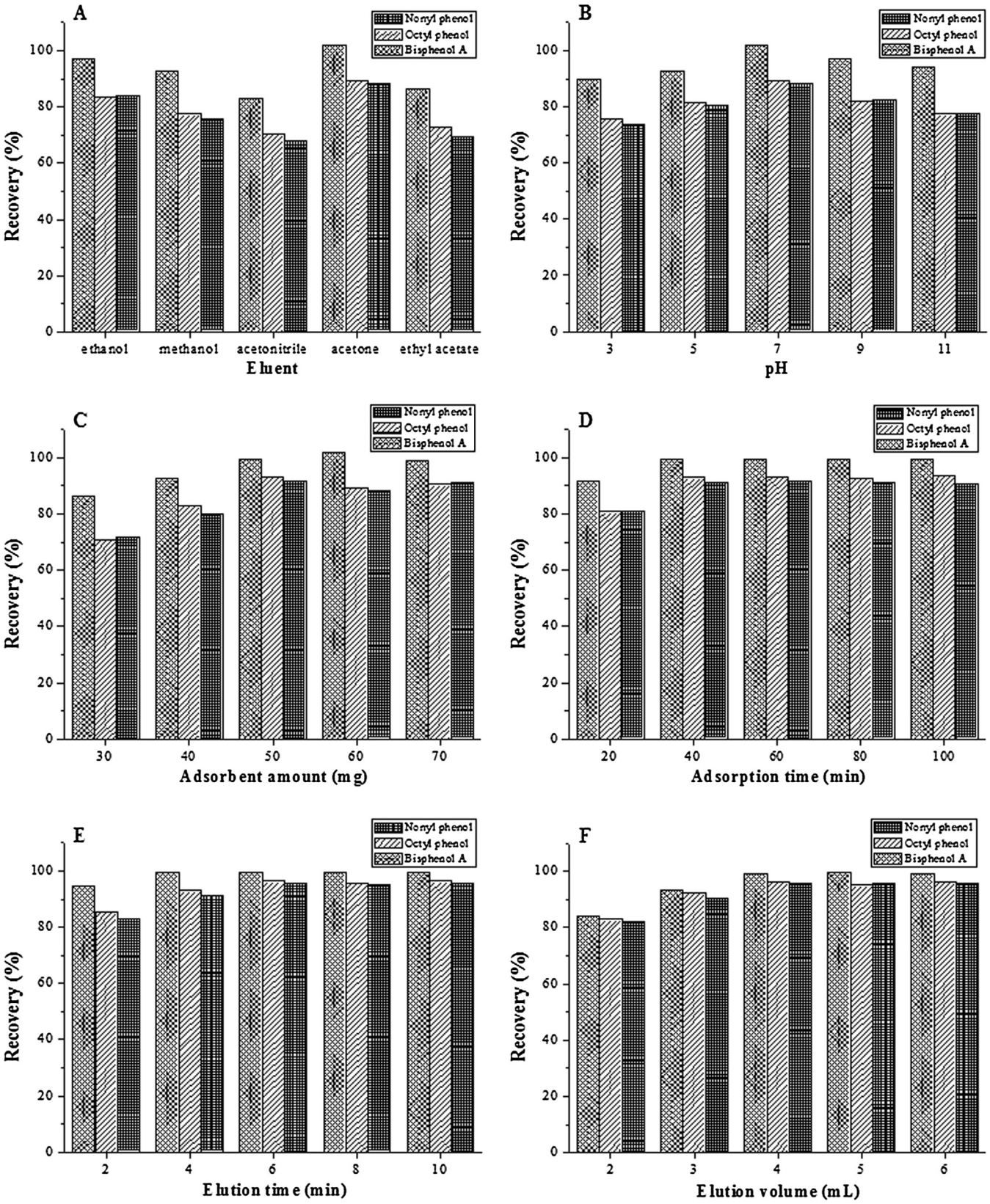

Fig. 4. Optimization of the important parameters. (A) Eluent; (B) sample pH; (C) Fe@MgAl-LDH amount; (D) adsorption time; (E) elution time; (F) eluent volume, (G) humic acid and (H) sample volume.

adsorbent. In this experiment, the adsorption time was investigated varying from 20 to 100 min with other conditions being held constant. As can be seen in Fig. 4D, the recoveries of BPA, 4-OP, 4-NP increased and reached the maxima with recoveries of BPA up to almost 100% and recoveries over 90% for 4-OP and 4-NP, when the adsorption time increased to 40 min and then remained

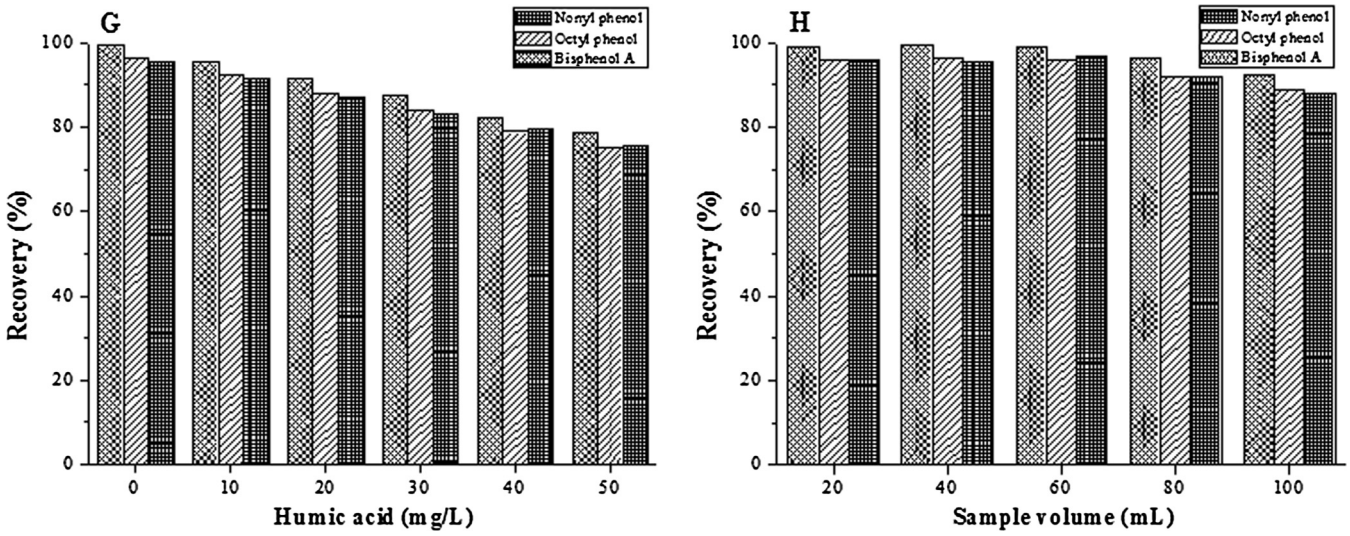

Fig. 4 (*continued*)

almost constant when the adsorption time increased from 40 min to 100 min. As known, the MSPE is an adsorption equilibrium process and the diffusion rate of the analytes onto the surface of adsorbent was larger than the desorption rate of the analytes from the surface of adsorbent, and the adsorbed analytes increased before the adsorption reaches equilibrium. When the equilibrium reached, the amount of analytes absorbed would be a constant value. Therefore, 40 min was selected as the adsorption time for the following experiments.

Elution is another important step in MSPE, which is also related to the MSPE performance. Elution time was investigated varying from 2 to 10 min. It was found that with the increase of elution time, the recoveries of three analytes increased and reached maximum values when the elution time was 6 min (see Fig. 4E), and the recoveries have no significant change with the continuous increase of elution time. These results indicated that three phenols had been effectively desorbed from the adsorbents when elution time was over 6 min. Therefore, 6 min was used for elution in the following experiments. The volume of elution solvent also plays an important role in the MSPE procedure, which determines whether the analytes are eluted completely or not. In order to obtain a reasonable volume of acetone to eluent all of three analytes from Fe@MgAl-LDH, the volume of acetone was optimized in the range of 2–6 mL. As seen in Fig. 4F, the quantitative recoveries of BPA, 4-OP and 4-NP (99%, 96% and 95%, respectively) could be achieved when the volume of acetone was in the range of 4–6 mL, and the difference of recoveries was very small for each analyte. The best elution performance was achieved with 4 mL acetone for 4 times with 1 mL each time (90 s, each time). When the volume of acetone was less than 4 mL, the absorbed analytes were incompletely eluted from Fe@MgAl-LDH. Based on these, 4 mL acetone was selected as the eluent.

Salting-out effect is often utilized to increase the recoveries of target analytes and further increase the sensitivity of the established method, especially for MSPE and liquid phase microextraction. Salting-out effect is realized by adjusting the ionic strength of the sample solution. Herein, salting-out effect on the recoveries of BPA, 4-OP, 4-NP was evaluated by adjusting the salinity of solution with NaCl in the concentration range of 0–25% (w/v). The results showed that the effect was a negative effect on the recoveries of three phenols, the recoveries decreased with the increase of NaCl concentration. The reason may be that the increase of the iron strength could reduce the hydrogen bond or hydrophilic interaction force. Hence, NaCl was not added for the subsequent experiments.

Humic acid is a natural organic material in the water system, and which will affect the enrichment performance. It was optimized in the range of 0–50 mg L^{-1}. As shown in Fig. 3G, the recoveries of the analytes decreased slowly with the increase of humic acid concentration. The reason may be that humic acid can adsorb onto the adsorbents and result in reduction of adsorption sites, and which leads to the decrease of adsorption ability.

Sample volume is another important parameter in MSPE procedure, which is also a simple way to obtain high sensitivity by increasing the sample volume. In this study, sample volume was evaluated in the range of 20–100 mL. The results exhibited that the recoveries had no significant change in the range of 20–60 mL, yet decreased slowly when the sample volume increased continuously (see Fig. 3H). Therefore, to get the higher enrichment factor, 60 mL was selected in subsequent experiments (enrichment factor = 300).

3.3. Reusability of the adsorbent

Reusability is one of the important factors for evaluation of adsorption performance. In order to examine reusability of Fe@MgAl-LDH, the used Fe@MgAl-LDH adsorbents were washed several times with acetone and water, and then dried for reuse. After ten times of reusing, there was no obvious change in the recoveries of the analytes. The recoveries were in the range of 98.7–99.9% for BPA, 94.7–96.9% for 4-OP and 94.2–98.1% for 4-NP. The results indicated that Fe@MgAl-LDH was stable in the MSPE procedure and had good reusability. The TEM images of Fe@MgAl-LDH magnetic particles after using also confirmed the stability of Fe@MgAl-LDH (see Fig. 2B).

3.4. Method validation and analysis of environment water samples

Under the optimum experimental conditions, calibration curves of the analytes were established in the range of 0.5–200 μg L^{-1}. The parameters including linear range, correlation coefficient, relative standard deviation and limit of detection were listed in Table 1. It can be seen that all the analytes had good linearities with the correlation coefficient (r) > 0.999. The detection limits (S/N = 3) of all analytes were ranged in 0.2–0.4 μg L^{-1}. The RSDs for all analytes were below 3%.

Table 1
Analytical parameters of the proposed method.

Analytes	Linearity range (μg L^{-1})	Correlation coefficient (r)	RSD (%) (n = 6)	Detection limit (μg L^{-1})
Bisphenol A	0.5–200	0.999	1.24	0.24
4-Octyl phenol	0.5–200	0.999	2.30	0.33
4-Nonyl phenol	0.5–200	0.999	2.12	0.34

Table 2
Results of spiked and blank real water samples.

Water sample	Spiked (μg L^{-1})	Recovery (%)		
		Bisphenol A	Octyl phenol	Nonyl phenol
Nanshahe River water	0	nd	nd	nd
	5	98.9 ± 0.2[a]	96.3 ± 0.2	96.0 ± 0.1
	10	99.3 ± 0.3	96.2 ± 0.2	96.5 ± 0.2
Huchenghe River water	0	nd	nd	nd
	5	98.7 ± 0.1	96.6 ± 0.2	96.0 ± 0.1
	10	99.2 ± 0.2	96.3 ± 0.1	96.4 ± 0.1
Gaobeidian wastewater	0	nd	nd	nd
	5	98.9 ± 0.2	96.8 ± 0.2	96.0 ± 0.1
	10	99.3 ± 0.1	96.2 ± 0.1	96.4 ± 0.1
Changping Park water	0	nd	nd	nd
	5	99.1 ± 0.2	96.3 ± 0.1	96.1 ± 0.2
	10	99.3 ± 0.2	96.2 ± 0.1	96.2 ± 0.1

nd: not detected; a, mean recovery ± standard deviation(n = 3).

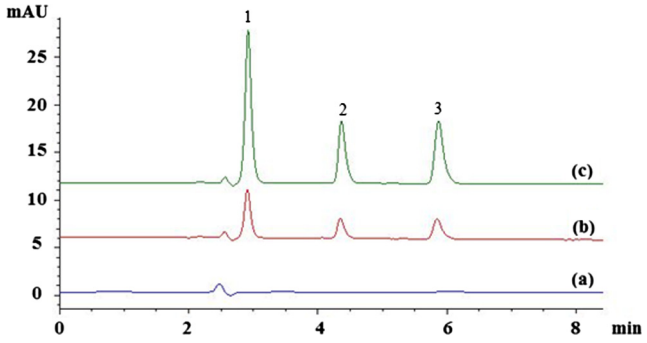

Fig. 5. HPLC chromatogram of environmental water samples obtained from MSPE with Fe@MgAl-LDH. (a) Blank of Nanshahe River water; (b) spiked water, spiked concentration: 5 μg L^{-1}; (c) spiked water, spiked sample concentration: 10 μgL^{-1}. Peak identification: 1, BPA; 2, 4-OP; 3, 4-NP.

To examine the applicability of developed method, real water samples from Nanshahe River, Huchenghe River, Gaobeidian wastewater and Changping Park River were analyzed. None of the three analytes were detected in the blank water samples. Spiked water samples were also analyzed and the results were shown in Table 2. The chromatogram of blank and spiked environmental water samples were shown in Fig. 5. As observed from Table 2, all the recoveries were in the range of 96.0–99.3%, which indicated that Fe@MgAl-LDH was a good adsorbent for these three phenols and would have good applications in the analysis of real water samples.

To evaluate the proposed method, it was compared with other methods reported in the literatures [43–48] for the determination of BPA, 4-OP and 4-NP. The data in Table 3 showed present method was better than or comparable with reported microporous bamboo charcoal based solid phase extraction, temperature-controlled ionic liquid dispersive liquid-phase microextraction, hybrid solid phase extraction-precipitation technology and C18 cartridges based solid phase extraction. Obviously, our micro-SPE method based on magnetic nanomaterials can make separation process easier and faster, thereby attain higher separation efficiency.

4. Conclusions

Present study provided an efficient adsorbent, MgAl-layered double hydroxide (MgAl-LDH) modified nanoscale zero-valent iron (NZVI) particles, for magnetic solid phase extraction followed by high performance liquid chromatography coupled with variable wavelength detection to determine BPA, 4-OP, 4-NP from water samples. The Fe@MgAl-LDH nanoparticles demonstrated good enrichment ability for BPA, 4-OP, 4-NP, and the established method resulted in low limits of detection in the range of 0.24–0.34 μg L^{-1} and good linearity in the range of 0.5–200 μg L^{-1} with the correlation coefficients (r) above 0.999. The proposed method

Table 3
Comparison of the proposed method with reported methods for determination of bisphenol A, 4-octylphenol and 4-nonylphenol.

Methods	Analytes	Detection	Matrice	Linear ranges (μg L^{-1})	LODs (μg L^{-1})	Ref.
OASIS HLB cartridges based SPE	BPA, 4-OP, 4-NP	UPLC-MS	Urine	1.0–500	0.1–0.15	[45]
Multiwalled carbon nanotubes based SPE	BPA, 4-OP, 4-NP	HPLC-FLD	Water sample	0.2–200	0.018–0.024	[46]
Microporous bamboo charcoal based SPE	BPA, 4-OP, 4-NP	HPLC-UV	Water sample	2–100	0.17–0.37	[47]
Temperature-controlled ionic liquid dispersive liquid-phase microextraction	BPA, 4-OP, 4-NP	HPLC-FLD	Water sample	1–300	0.23–0.48	[48]
Hybrid SPE-precipitation technology	BPA, 4-OP, 4-NP	LC-MS/MS	Serum	1–100	0.8–1.4	[49]
C18 cartridges based SPE	BPA, 4-OP, 4-NP	HPLC-MS/MS	Urine	1–100	0.15–0.32	[50]
Fe@MgAl-LDH based SPE	BPA, 4-OP, 4-NP	HPLC-VWD	Water sample	0.5–200	0.24–0.34	This method

was validated with real water samples and satisfied spiked recoveries were achieved. These indicated that Fe@MgAl-LDH had great potential application in the future.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21377167).

References

[1] N. Salgueiro-González, I. Turnes-Carou, S. Muniategui-Lorenzo, P. López-Mahía, D. Prada-Rodríguez, Fast and selective pressurized liquid extraction with simultaneous in cell clean-up for the analysis of alkylphenols and bisphenol A in bivalve molluscs, J. Chromatogr. A 1270 (2012) 80–87.
[2] N. Salgueiro-González, E. Concha-Graña, I. Turnes-Carou, S. Muniategui-Lorenzo, P. López-Mahía, D. Prada-Rodríguez, Blank and sample handling troubleshooting in ultratrace analysis of alkylphenols and bisphenol A by liquid chromatography tandem mass spectrometry, Talanta 101 (2012) 413–419.
[3] H. Huang, Y. Li, J. Liu, J. Tong, X. Su, Detection of bisphenol A in food packaging based on fluorescent conjugated polymer $PPESO_3$ and enzyme system, Food Chem. 185 (2015) 233–238.
[4] X. Zhang, D. Zhu, C. Huang, Y. Sun, Y.I. Lee, Sensitive detection of bisphenol A in complex samples by in-column molecularly imprinted solid-phase extraction coupled with capillary electrophoresis, Microchem. J. 121 (2015) 1–5.
[5] R.B.P. Vidal, G.A. Ibañez, G.M. Escandar, Chemometrics-assisted cyclodextrin–enhanced excitation–emission fluorescence spectroscopy for the simultaneous green determination of bisphenol A and nonylphenol in plastics, Talanta 143 (2015) 162–168.
[6] K. Li, D. Wei, G. Zhang, L. Shi, Y. Wang, B. Wang, X. Wang, B. Du, Q. Wei, Toxicity of bisphenol A to aerobic granular sludge in sequencing batch reactors, J. Mol. Liq. 209 (2015) 284–288.
[7] Chinese standard for drinking water GB5749-2006.
[8] M. Staniszewska, I. Koniecko, L. Falkowska, E. Krzymyk, Occurrence and distribution of bisphenol A and alkylphenols in the water of the gulf of Gdansk (Southern Baltic), Mar. Pollut. Bull. 91 (2015) 372–379.
[9] O. Ros, A. Vallejo, L. Blanco-Zubiaguirre, M. Olivares, A. Delgado, N. Etxebarria, A. Prieto, Microextraction with polyethersulfone for bisphenol-A, alkylphenols and hormones determination in water samples by means of gas chromatography-mass spectrometry and liquid chromatography-tandem mass spectrometry analysis, Talanta 134 (2015) 247–255.
[10] Ambient aquatic life water quality criteria for nonylphenol, Report for the United States EPA, Office of Water, Office of Science and Technology, Washington DC, USA, 2005
[11] Y. Cui, J. Zhao, J. Wang, H. Yu, X. Piao, D. Li, Water-based gas purge microsyringe extraction coupled with liquid chromatography for determination of alkylphenols from sea food Laminaria japonica Aresh, J. Chromatogr. A 1300 (2013) 38–42.
[12] N. Salgueiro-González, I. Turnes-Carou, S. Muniategui-Lorenzo, P. López-Mahía, D. Prada-Rodríguez, Pressurized hot water extraction followed by miniaturized membrane assisted solvent extraction for the green analysis of alkylphenols in sediments, J. Chromatogr. A 1383 (2015) 8–17.
[13] L. Min, Y. Hashi, F. Pan, J. Yao, G. Song, J.M. Lin, Automated on-line liquid chromatography-photodiode array-mass spectrometry method with dilution line for the determination of bisphenol A and 4-octylphenol in serum, J. Chromatogr. A 1133 (2006) 142–148.
[14] M. Cui, J. Qiu, Z. Li, M. He, M. Jin, J. Kim, M. Quinto, D. Li, An etched stainless steel wire/ionic liquid-solid phase microextraction technique for the determination of alkylphenols in river water, Talanta 132 (2015) 564–571.
[15] T. Geens, H. Neels, A. Covaci, Sensitive and selective method for the determination of bisphenol-A and triclosan in serum and urine as pentafluorobenzoate-derivatives using GC-ECNI/MS, J. Chromatogr. B 877 (2009) 4042–4046.
[16] F. Wang, J. Yang, K. Wu, Mesoporous silica-based electrochemical sensor for sensitive determination of environmental hormone bisphenol A, Anal. Chim. Acta 638 (2009) 23–28.
[17] T.F. Tsai, M.R. Lee, Liquid-phase microextraction combined with liquid chromatography-electrospray tandem mass spectrometry for detecting diuretics in urine, Talanta 75 (2008) 658–665.
[18] M.A. Farajzadeh, B. Feriduni, M.R.A. Mogaddam, Development of counter current salting-out homogenous liquid-liquid extraction for isolation and preconcentration of some pesticides from aqueous samples, Anal. Chim. Acta 885 (2015) 122–131.
[19] A. Combes, S. Pavel, P. Julia, N. Lucie, P. Valérie, Synthesis of a molecularly imprinted sorbent for selective solid-phase extraction of β-N-methylamino-l-alanine, Talanta 144 (2015) 1021–1029.
[20] C. Giovannoli, C. Passini, G. Volpi, F.D. Nardo, L. Anfossi, C. Baggiani, Peptide-based affinity media for solid-phase extraction of Ochratoxin A from wine samples: effect of the solid support on binding properties, Talanta 144 (2015) 496–501.
[21] A. Amini, Y. Kim, J. Zhang, T. Boyer, Q. Zhang, Environmental and economic sustainability of ion exchange drinking water treatment for organics removal, J. Clean. Prod. 104 (2015) 413–421.
[22] G.J. Millar, S.J. Couperthwaite, M.D. Bruyn, C.W. Leung, Ion exchange treatment of saline solutions using Lanxess S108H strong acid cation resin, Chem. Eng. J. 280 (2015) 525–535.
[23] S.C. Foo, F.M. Yusoff, M. Ismail, M. Basri, N.M.H. Khong, K.W. Chan, S.K. Yau, Efficient solvent extraction of antioxidant-rich extract from a tropical diatom, Chaetoceros calcitrans (Paulsen) Takano, Asian Pac. J. Trop. Biomed. 5 (2015) (1968) 834–840.
[24] T.H. Nguyen, M.S. Lee, Solvent extraction of vanadium (V) from sulfate solutions using LIX 63 and PC 88A, J. Ind. Eng. Chem. 31 (2015) 118–123.
[25] R.M.P. Crecente, C.G. Lovera, J.B. García, C.H. Latorre, Ultrasound-assisted magnetic solid-phase extraction for the determination of some transition metals in Orujo spirit samples by capillary electrophoresis, Food Chem. 190 (2015) 263–269.
[26] F. Omidi, M. Behbahani, M.K. Bojdi, S.J. Shahtaheri, Solid phase extraction and trace monitoring of cadmium ions in environmental water and food samples based on modified magnetic nanoporous silica, J. Magn. Magn. Mater. 395 (2015) 213–220.
[27] M.M. Tian, D.X. Chen, Y.L. Sun, Y.W. Yang, Q. Jia, Pillararene-functionalized Fe_3O_4 nanoparticles as magnetic solid-phase extraction adsorbent for pesticide residue analysis in beverage samples, RSC Adv. 3 (2013) 22111–22119.
[28] S. Zeng, G. Ning, R. Weideman-Mera, Y. Cao, T. Li, W. Sang, Enrichment of polychlorinated biphenyl 28 from aqueous solutions using Fe_3O_4 grafted graphene oxide, Chem. Eng. J. 218 (2013) 108–115.
[29] J. Yang, J.Y. Li, J.Q. Qiao, S.H. Cui, H.Z. Lian, H.Y. Chen, Magnetic solid phase extraction of brominated flame retardants and pentachlorophenol from environmental waters with carbon doped Fe_3O_4 nanoparticles, Appl. Surf. Sci. 321 (2014) 126–135.
[30] L. Lan, B. Pan, W.X. Zhang, Removal of selenium from water with nanoscale zero-valent iron: mechanisms of intraparticle reduction of Se(IV), Water Res. 71 (2015) 274–281.
[31] X. Zhou, B. Lv, Z. Zhou, W. Li, G. Jing, Evaluation of highly active nanoscale zero-valent iron coupled with ultrasound for chromium (VI) removal, Chem. Eng. J. 281 (2015) 155–163.
[32] H. Dong, G. Zeng, C. Zhang, J. Liang, K. Ahmad, P. Xu, X. He, M. Lai, Interaction between Cu^{2+} and different types of surface-modified nanoscale zero-valent iron during their transport in porous media, J. Environ. Sci. 32 (2015) 180–188.
[33] L.N. Shi, Z. Xin, Z.L. Chen, Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron, Water Res. 45 (2011) 886–892.
[34] F. Liu, J.H. Yang, J. Zuo, M. Ding, L. Gan, B. Xie, W. Pei, Y. Bo, Graphene-supported nanoscale zero-valent iron: Removal of phosphorus from aqueous solution and mechanistic study, J. Environ. Sci. 26 (2014) 1751–1762.
[35] J. Wang, R. Zhu, B. Gao, B. Wu, K. Li, X. Sun, H. Liu, S. Wang, The enhanced immune response of hepatitis B virus DNA vaccine using SiO_2@LDH nanoparticles as an adjuvant, Biomaterials 35 (2014) 466–478.
[36] Y. Wang, Y. Zhou, T. Zhang, M. He, X. Bu, Fabrication of core-shell structural SiO_2@DNA-LDH nanocomposite with low infrared emissivity, Chem. Eng. J. 266 (2015) 199–202.
[37] S. Tang, G.H. Chia, Y.P. Chang, H.K. Lee, Automated dispersive solid-phase extraction using dissolvable Fe_3O_4-layered double hydroxide core-shell microspheres as sorbent, Anal. Chem. 86 (2014) 11070–11076.
[38] T. Bujdosó, Á. Patzkó, Z. Galbács, I. Dékány, Structural characterization of arsenate ion exchanged MgAl-layered double hydroxide, Appl. Clay Sci. 44 (2009) 75–82.
[39] B. Wang, Z. Hui, D.G. Evans, D. Xue, Surface modification of layered double hydroxides and incorporation of hydrophobic organic compounds, Mater. Chem. Phys. 92 (2005) 190–196.
[40] I.M. Ahmed, M.S. Gasser, Adsorption study of anionic reactive dye from aqueous solution to Mg-Fe-CO_3 layered double hydroxide (LDH), Appl. Surf. Sci. 259 (2012) 650–656.
[41] Y. You, H. Zhao, G.F. Vance, Surfactant-enhanced adsorption of organic compounds by layered double hydroxides, Colloid Surf. A 205 (2002) 161–172.
[42] X. Chen, F. Mi, H. Zhang, H. Zhang, Facile synthesis of a novel magnetic core-shell hierarchical composite submicrospheres Fe_3O_4@CuNiAl-LDH under ambient conditions, Mater. Lett. 69 (2012) 48–51.
[43] A. Legrouri, M. Lakraimi, A. Barroug, A.D. Roy, J.P. Besse, Removal of the herbicide 2,4-dichlorophenoxyacetate from water to zinc-aluminium-chloride layered double hydroxides, Water Res. 39 (2005) 3441–3448.
[44] B. Qi, D. Li, X. Ni, H. Zheng, A facile chemical reduction route to the preparation of single-crystalline iron nanocubes, Chem. Lett. 36 (2007) 722–723.
[45] Y. Wu, A study on bisphenol a, nonylphenol and octylphenol in human urine samples detected by SPE-UPLC-MS, Biomed. Environ. Sci. 24 (2011) 40–46.
[46] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, Multiwalled carbon nanotubes as a solid-phase extraction adsorbent for the determination of bisphenol a, 4-n-nonylphenol, and 4-tert-octylphenol, Anal. Chem. 75 (2003) 2517–2521.
[47] R.S. Zhao, X. Wang, J.P. Yuan, L.L. Zhang, Solid-phase extraction of bisphenol A, nonylphenol and 4-octylphenol from environmental water samples using microporous bamboo charcoal, and their determination by HPLC, Microchim. Acta 165 (2009) 443–447.
[48] Q.X. Zhou, Y.Y. Gao, G.H. Xie, Determination of bisphenol A, 4-n-nonylphenol, and 4-tert-octylphenol by temperature-controlled ionic liquid dispersive liquid-phase microextraction combined with high performance liquid chromatography-fluorescence detector, Talanta 85 (2011) 1598–1602.

[49] A.G. Asimakopoulos, N.S. Thomaidis, Bisphenol A, 4-t-octylphenol, and 4-nonylphenol determination in serum by hybrid solid phase extraction–precipitation technology technique tailored to liquid chromatography–tandem mass spectrometry, J. Chromatogr. B 986–987 (2015) 85–93.

[50] F. Zhou, Z. Lin, L. Ai, S. Yang, J. Yuan, X. Yu, F. Xu, X. Qian, C. Cheng, Measurement of phenolic environmental estrogens in human urine samples by HPLC–MS/MS and primary discussion the possible linkage with uterine leiomyoma, J. Chromatogr. B 938 (2013) 80–85.