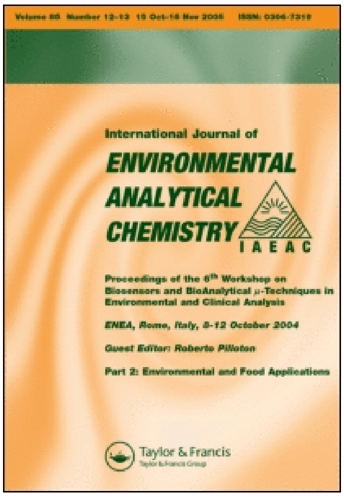

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The aim of this paper is to test the feasibility of multiwalled carbon nanotubes (MWCNTs) and cigarette filters (CGFRs) as solid adsorbents for pre-concentration of DBP and DEHP in water; and to compare with C_{18} to investigate which has the best enrichment factor. It was found that cigarette filters exhibited the better recoveries and were therefore the best solid sorbent of the three materials tested, while multiwalled carbon nanotubes were unsuitable for enriching DBP and DEHP on account of its low recoveries. Parameters that may influence the extraction efficiency such as the eluent volume, sample flow rate, sample pH, and the sample volume were optimized. The results showed that the precisions (relative standard deviation, RSD) were 1.40% and 1.72% for DBP and DEHP under the optimal conditions. The detection limits of the developed method could reach 3.1 ng L^{-1} and 4.3 ng L^{-1} for DBP and DEHP, respectively, based on the ratio of the chromatographic signal to base line noise (S/N = 3). Satisfactory results were achieved when the proposed method was applied to determine the two target compounds in drinking water with spiked recoveries in the range of 93.6–98.7%. The results indicated that CGFR was a significantly better sorbent to enrich DBP and DEHP in drinking water than the other solid sorbents.

Keywords: multiwalled carbon nanotubes; cigarette filter; high performance liquid chromatography; di-butylphthalate; di-2-ethylhexylphthalate; drinking water

1. Introduction

DBP and DEHP are potentially harmful chemicals to human health [1] as they are readily released into the environment through volatilization and leaching from plastics and other sources. Their widespread usage coupled with their stability has made them ubiquitous environmental contaminants. Phthalic acid esters, which have almost no acute toxicity, have been attached a certain importance for their subacute and chronic toxicity. Subacute toxicity experiments in animals showed that phthalic acid ester exposure could lead to avoirdupois decline, leukocytosis, anemia, hematuria; and especially harm to the liver [2]. At present, plastics are widely used in the packaging of drinking water, and as such, there is the possibility that phthalic acid esters may leach from the packaging to contaminate the water. In China, the groundwater of some areas has been polluted by phthalic acid

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esters [3]. To safeguard human health, the WHO has established safe maximum contaminant levels (MCLs) for di-2-ethylhexylphthalate at the level of $0.006\,\mathrm{mg\,L^{-1}}$. Therefore, it is very important to develop a method to detect their residues.

Nowadays, various chromatographic methods including gas chromatography with flame ionization or electron-capture detection [4], and high-performance liquid chromatography (HPLC), have been developed for the analysis of chemicals such as DBP and DEHP. These procedures all have obvious advantages and limitations in terms of specificity, sensitivity and measurement times. In the process of determination, the pretreatment of the samples is the key step effecting determination. Solid-phase extraction (SPE) using a conventional bonded silica sorbent has been applied for the isolation and trace enrichment of organic contaminants from environmental samples before their analysis by chromatographic techniques [5]. In this study, MWCNTs, CGFR and C_{18} used as solid-phase extraction materials were used to pretreat samples. C_{18} has been used as a solid-phase extraction material in the analysis of both DBP and DEHP [5]. It is well known that CGFR, of which the main component is cellulose acetate, can efficiently adsorb many poisonous organic compounds and, hence, alleviate their poisonous effect on smokers [6]. CGFR has been successfully used as the sorbent for the pre-concentration and separation of the MeHg-DDTC and Hg-APDC chelates, and polycyclic aromatic hydrocarbons [6,7]. Carbon nanotubes (CNTs), which are novel carbon materials [8], can be divided into single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) [9] according to the carbon atom layers in the wall of the nanotubes. MWCNTs have great analytical potential as an effective solid-phase extraction adsorbent for chelates or ion pairs of metal ions, organic compounds, and organometallic compounds [10,11] MWCNTs have been successfully used as the sorbent for the pre-concentration and separation of dioxins [12], bisphenol A [13], and phthalate esters [14]. Although MWCNTs have been used as solid phase materials to extract phthalate esters from water samples [14], to our knowledge, the application of MWCNTs and CGFR as sorbent materials on the DBP and DEHP analysis in drinking water has not been reported.

The aims of this study were to evaluate different sorbents for the determination of DBP and DEHP from drinking water and to develop a method for the determination of DBP and DEHP in drinking water. The sorbents were tested to determine which of them was the most appropriate for the pre-concentration of the analytes. MWCNTs and CGFR, presented in a disposable cartridge, were evaluated and compared with a conventional C_{18} silica-bonded sorbent.

2. Method

2.1 *Apparatus*

The high-performance liquid chromatographic system consisted of two Lc-10ATvp pumps on an analytical reversed-phase column (Shimadzu-C_{18}, 5 µm, 4.6 mm × 150 mm, Shimadzu, Japan) at a mobile flow rate of $1.0\,\mathrm{mL\,min^{-1}}$ under isocratic conditions at a column temperature of 40°C. Class-VP software was used to acquire and process spectral and chromatographic data. The ultraviolet detector was operated at 230 nm.

2.2 *Materials and reagents*

MWCNTs with an average diameter of 60–100 nm, length of 5–15 µm and surface area of $40\text{–}300\,\mathrm{m^2\,g^{-1}}$ were obtained from Shenzhen Nanotechprot Co. Ltd, Shenzhen, China.

Cigarette filters were obtained from the Kunming Cigarette Factory, Yunnan Province, China. All reagents were of the highest available purity and at least analytical grade. Double deionized water (DDW, 18.2 $\mathrm{M\Omega\,cm^{-1}}$) was obtained from Waterpro. A water system (Labconco Corporation, Kansas City, Mo, USA) was used throughout the experiments. Methanol purchased from Merck Germany was used as the mobile-phase. N_2 was used for sample pretreatment. DBP and DEHP were purchased from the National Research Center for CRMs of China. Stock solutions of DBP and DEHP were prepared by dissolving 10 mg of DBP and DEHP in 10 ml methanol and then stored at 4°C in the dark. Fresh stock solutions were prepared weekly and stored at 4°C in the dark. The working solutions were adjusted by diluting the fresh stored solution with DDW. The cartridges used for the pre-concentration step were 3 mL disposable extraction syringes packed with 200 mg Strata Scx C_{18} E from Phenomenex.

2.3 *Backfilling and preconditioning solid-phase extraction column*

The empty SPE cartridge was filled with 60 mg multiwalled carbon nanotubes (MWCNTs) or cigarette filters (CGFRs). The columns filled with MWCNTs were conditioned with 200 mL DDW, 100 mL methanol, and then 50 mL DDW. Preliminary experiments showed that CGFR was not adequately cleaned when treated following the same procedure for the MWCNTs cartridges. Therefore, the cigarette filter cartridges were cleaned with 200 mL DDW, 400 mL methanol, then 50 mL DDW. The C_{18} sorbent was conditioned with 3 mL DDW, 3 mL methanol, and 3 mL DDW and then used for the prepared samples.

2.4 *Sample pretreatment*

Drinking water samples were filtered through 0.45 µm super filters, stored in precleaned glass bottles (thoroughly washed with detergents, water, methanol, and doubly deionized water, and dried before use). The water samples were then passed through the C_{18}-SPE or the extraction cartridge packed with MWCNTs or CGFR at a flow rate of 3.5 $\mathrm{mL\,min^{-1}}$ on a vacuum manifold. The analytes were eluted with 4 mL of methanol into a test tube. The extracts were blown dry under a flow of N_2 gas at room temperature, then, 1 mL of methanol was added and 20 µL of the sample was injected into the HPLC system for analysis.

2.5 *Procedure for the validation of the entire method*

For the validation of the method proposed in this study, 50 mL blank samples were spiked with 1 mL of the analytes. The concentrations of the analytes in the spiked samples were 5 $\mathrm{\mu g\,L^{-1}}$, 1 $\mathrm{\mu g\,L^{-1}}$ and 1 $\mathrm{\mu g\,L^{-1}}$, respectively. The other steps of the analysis were the same as described in the previous section.

3. Results and discussion

3.1 *Optimization of the extraction conditions of the three materials*

Trace analysis by the HPLC method is affected by co-extracted substances causing a severe baseline deviation. For this reason it is necessary to clean-up the sample before the

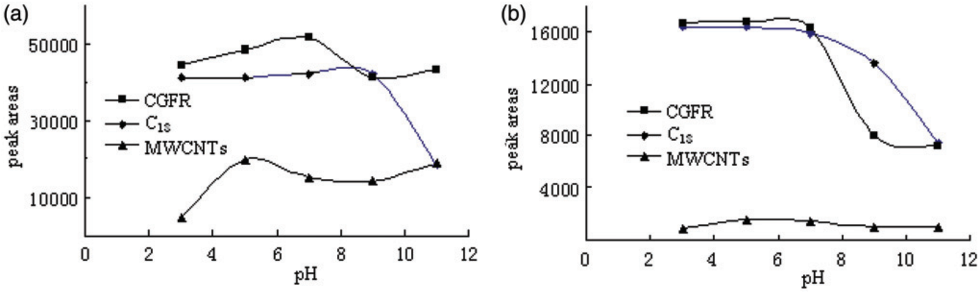

Figure 1. Effect of pH on the adsorption of (a) DBP and (b) DEHP by using CGFR-, MWCNT- and C_{18}-packed cartridges.

HPLC analysis. SPE sorbents provide a method allowing the simultaneous enrichment and clean-up of organic pollutants in water samples [15]. In order to select the best sorbent for the pre-concentration of DBP and DEHP, multiwalled carbon nanotubes, cigarette filters, and a commercially available SPE (C_{18} silica sorbent) were evaluated.

The chemical and flow variables, such as sample acidity, sample loading flow rate and loading time, eluent and its concentration and flow rate, were optimized to achieve good sensitivity and precision for the extraction and elution of DBP and DEHP. The sample acidity and loading flow rates were optimized to choose the most suitable condition for three extraction materials to extract DBP and DEHP. The ester-group of the phthalic acid molecule may undergo hydrolysis in acid or alkaline conditions. The hydrolysis is reversible and incomplete in acidic environments, but non-reversible in alkaline environments, because the products of the hydrolysis are the stable carboxylic acid ion and alcohol molecule. The hydrolysis reaction occurs in a negative direction, because the DBP and DEHP are absorbed by the solid-phase materials when the acid sample is flowed through the SPE cartridge. 50 mL samples of DBP and DEHP mixtures ($5\,\mu g\,L^{-1}$) having different pH values were enriched. After desorption with methanol under optimized conditions and concentrations, DBP and DEHP were then detected by HPLC. Using the calculated peak areas as the Y-axis and pH as the X-axis, a curve of the pH effect on the enrichment performance was achieved. As shown in Figure 1, the absorbent effect of the three sorbents did not show obvious changes when the pH of the samples was below 7, but declined obviously because of the formation of carboxylic acid ions in alkaline environments.

The loading flow rate during the adsorption step is an important parameter to be evaluated in the SPE procedure. The flow rate of the sample solution not only affects the recovery of analytes, but also controls the analysis time. In our studies, duplicate measurements indicated that the flow rates did not significantly influence the extraction efficiency for the three solid-phase extraction materials. Based on the above results and considering the analysis time, the conditions of $pH = 7$ and sample loading flow rate of $3.5\,mL\,min^{-1}$ were chosen.

As DBP and DEHP were concerned, the use of different organic solvents as eluent would have different elution powers yielding different enrichment efficiencies. LC-grade acetonitrile and methanol were investigated. The experimental results demonstrated that DBP and DEHP could be eluted by both elutions. Considering the mobile-phase and the toxicity of acetonitrile, methanol was employed as the eluent in this study. The final

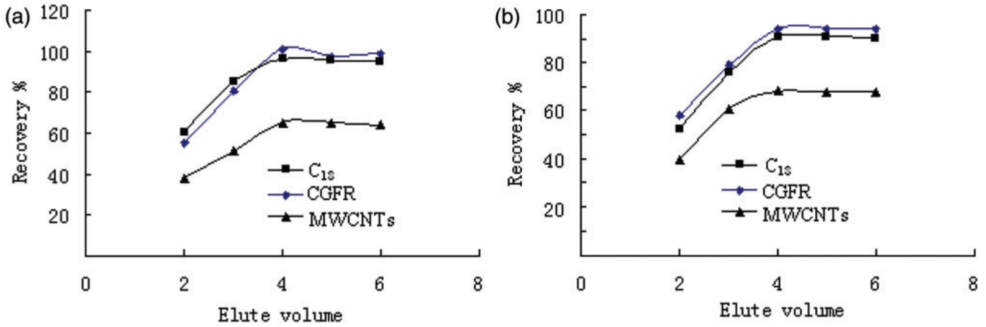

Figure 2. Effect of volume of eluent on the recoveries of (a) DBP and (b) DEHP by using CGFR-, MWCNT- and C_{18}-packed cartridges.

residue dissolved in methanol yielded a symmetrical peak shape. Aside from the fact that the kind of organic solvent affected the enrichment, the amount of eluent is also expected to affect the enrichment efficiency. In order to test the effect of the amounts of eluent, a series of experiments were designed based on changing the volume of eluent from 2 to 6 mL. When the experiment was operated, another 10 mL of methanol was flowed through the MWCNT-, CGFR-, and C_{18}-packed cartridges before the next procedure in order to get rid of the residues which may be adsorbed on the cartridges. As shown in Figure 2, the recoveries of DBP and DEHP increased with the increasing volume of methanol between 2 and 4 mL, however, the recoveries changed very little with the further increase of methanol volume up to 6 mL. Thus, 4 mL methanol was utilized in the following experiments in order to achieve complete elution of DBP and DEHP, while conserving time and reagents.

The sample volume is an important parameter that reflects the analyte retaining ability of the adsorbent. To investigate the influence of sample volume, the sample volume was changed over the range of 50–500 mL with spiked concentration at 5 $\mu g\,L^{-1}$. Since the C_{18} is a commercial solid sorbent, only MWCNTs and CGFR were tested in this experiment. The results were shown in Figure 3, and it was found that no variations of the recoveries of DBP and DEHP for CGFR occurred when the sample volume increased from 50–500 mL. However, the recoveries of DBP and DEHP for MWCNTs decreased as the sample volume exceeded 400 mL. Considering the analysis time, a volume of 50 mL was chosen as the final sample volume for the enrichment.

3.2 *Analytical performance*

The analytical parameters such as the linear range, detection limits and reproducibility were the characteristics of the developed method. Related studies were carried out carefully and the results were given in Table 1. Linear ranges were achieved by determining a series of purified water samples at different concentration. The detection limits of DBP and DEHP for three solid sorbents were obtained based on the signals of the three solids of the baseline noise (S/N = 3) for the extraction of a 50 mL water sample. The reproducibility for enrichment of 50 mL of spiked water sample was evaluated by calculating the relative standard deviation (RSD) of nine replicate runs of the procedures. The results for the three solid sorbents shown in Table 1 indicated that the precision was

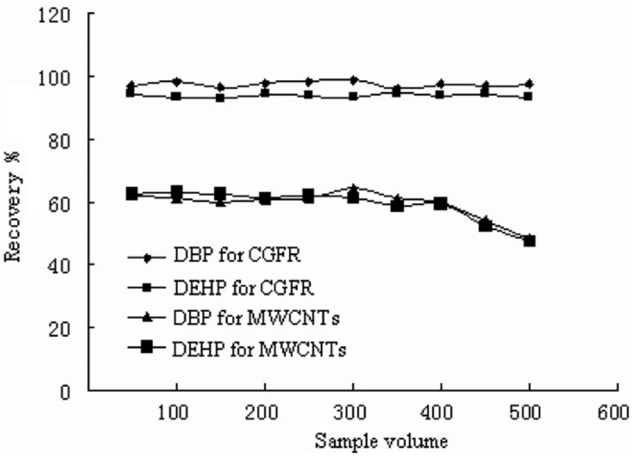

Figure 3. Effect of loading volume on the recoveries of DBP and DEHP using CGFR- and MWCNT-packed cartridges.

Table 1. Analytical parameters of developed method.

	Linear range ($\mu g\,L^{-1}$)		R^2		Reproducibility RSD% ($n = 9$)		Detection limits ($\mu g\,L^{-1}$)	
Solid sorbents	DBP	DEHP	DBP	DEHP	DBP	DEHP	DBP	DEHP
CGFR	0.3–70	0.3–70	0.9989	0.9991	1.4	1.7	0.0031	0.0043
C_{18}	0.3–70	0.3–70	0.9986	0.9993	1.5	1.9	0.0037	0.0041
MWNTs	0.5–60	0.5–60	0.9901	0.9932	2.0	3.6	0.0053	0.0064

satisfactory at low concentration ($5\,\mu g\,L^{-1}$) with RSDs in the range of 1.40–3.56% ($n = 9$) for DBP and DEHP.

The recoveries of DBP and DEHP for the three solid-phase materials from blank samples spiked at $5\,\mu g\,L^{-1}$, $10\,\mu g\,L^{-1}$ and $15\,\mu g\,L^{-1}$, respectively, were determined. At each concentration, three measurements were performed. The analytical procedure was operated under the optical conditions mentioned above. The data are reported in Table 2 and the typical chromatograms of real samples and real samples spiked at $5\,\mu g\,L^{-1}$ are shown in Figure 4. The recoveries of CGFR for DBP and DEHP were higher than those of C_{18} and MWCNTs, and it was easy to find that the spiked recoveries of CGFR for DBP and DEHP were in the range of 93.6% to 98.7%. However, the recoveries ranged from 59.7% to 63.0% of MWCNTs for DBP and DEHP did not satisfy the request of the experiment.

The interaction between carbon nanotubes and compounds may be attributed to physical adsorption. In the lacunaris structure MWCNTs, the adsorption sites are distributed on the inner and outer surfaces. The open tube structure of the MWCNTs with high specific surface area allows for a greater combinability and sorption of compounds [16]. Simultaneity, the closer the carbon atom layer interval of MWCNTs is, the lower the adsorption of compounds [17]. In our study, the average external diameter of the multiwalled carbon nanotubes obtained from Shenzhen Nanotechprot Co. Ltd,

Table 2. Recoveries of DBP and DEHP with three solid-phase extraction materials (Mean% (RSD), $n = 3$).

	Spiked levers ($\mu g\,L^{-1}$)					
	DBP			DEHP		
Solid sorbents	5	10	15	5	10	15
CGFR (%)	96.6 (0.8)	98.7 (1.2)	98.4 (2.1)	94.2 (3.9)	93.6 (2.9)	94.4 (1.7)
C_{18} (%)	94.8 (1.6)	90.1 (2.3)	96.8 (3.1)	92.0 (4.8)	91.9 (5.9)	90.2 (0.6)
Multiwalled carbon nanotubes (%)	59.7 (0.7)	60.3 (4.1)	61.6 (2.2)	61.1 (1.2)	63.0 (4.6)	60.4 (3.1)

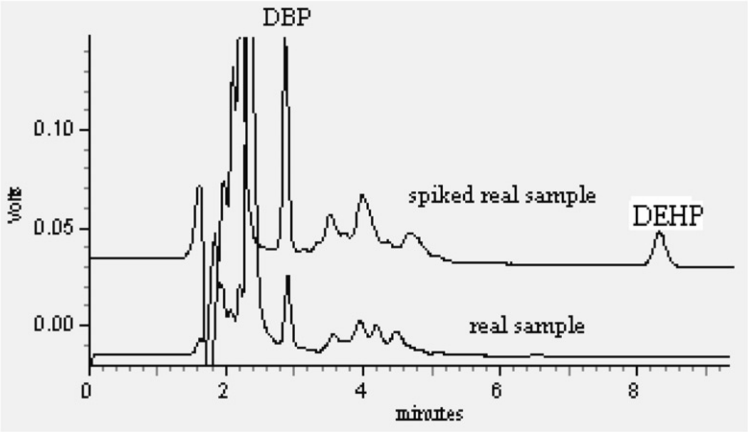

Figure 4. Chromatograms of a blank bottled drinking water sample and bottled drinking water sample spiked with $5\,\mu g\,L^{-1}$ of DBP and DEHP obtained by using CGFR-packed cartridges.

Shenzhen, China was 60–100 nm, however, those MWCNTs provided by Tsinghua-Nafine Nano-Power Commercialization Engineering Center, Chemical Engineering Department of Tsinghua University, Beijing, China were reported by Cai *et al.* to be 30–60 nm [14]. Therefore, it is considered that the different external diameters and productions of multiwalled carbon nanotubes may have different specific surface areas and carbon atom layer intervals. In this study, drinking water samples were used, while Cai *et al.* studied river water and sea water samples. The interference matrix in different samples can affect the enrichment performance of multiwalled carbon nanotubes. So these can be used to explain why the recoveries of MWCNTs for DBP and DEHP, which ranged from 59.7% to 63.0%, were not identical to that reported by Cai *et al* [14].

The above discussion shows that CGFR could effectively extract DBP and DEHP, and a good concentration effect could be obtained by this method. Furthermore, CGFR-packed cartridges for use as SPE could be reused, and it was found that the enrichment performance did not decline after the CGFR-packed cartridges were used for about 100 times in our study.

Table 3. Determination and recoveries spiked of 5 μg L^{-1} of DBP and D EHP in drinking water samples.

Water sample	Analytes	Found[a] (μg L^{-1}) Mean	Recoveries[b] mean% (RSD)	Water sample	Analytes	Found[a] (μg L^{-1}) Mean	Recoveries[b] mean% (RSD)
Bottled drinking water 1	DBP	0.73	97.2 (1.3)	Barrelled drinking water 1	DBP	nd	97.5 (4.3)
	DEHP	nd	93.8 (2.6)		DEHP	3.66	93.8 (2.1)
Bottled drinking water 2	DBP	0.81	96.8 (1.9)	Barrelled drinking water 2	DBP	nd	95.8 (1.8)
	DEHP	1.93	94.2 (2.3)		DEHP	2.28	92.8 (2.6)
Bottled drinking water 3	DBP	0.56	96.3 (1.6)	Barrelled drinking water 3	DBP	0.96	97.3 (3.6)
	DEHP	2.13	93.7 (2.7)		DEHP	2.42	92.6 (3.8)
Bottled drinking water 4	DBP	0.62	95.8 (1.2)	Barrelled drinking water 4	DBP	0.78	97.4 (2.7)
	DEHP	nd	93.6 (2.6)		DEHP	2.23	93.1 (2.9)
Bottled drinking water 5	DBP	nd	97.2 (3.5)	Barrelled drinking water 5	DBP	1.08	96.9 (3.7)
	DEHP	2.34	94.2 (3.7)		DEHP	2.35	92.8 (4.3)
Bottled drinking water 6	DBP	56.1	95.8 (1.8)	Barrelled drinking water 6	DBP	0.61	97.5 (4.1)
	DEHP	2.02	93.2 (3.8)		DEHP	2.24	93.2 (1.9)
Bottled drinking water 7	DBP	0.52	96.8 (4.2)	Barrelled drinking water 7	DBP	0.63	96.3 (3.3)
	DEHP	2.59	92.9 (5.1)		DEHP	2.38	93.4 (2.6)
Bottled drinking water 8	DBP	1.90	97.4 (2.9)	Barrelled drinking water 8	DBP	1.79	97.3 (3.6)
	DEHP	nd	93.1 (2.4)		DEHP	nd	92.4 (5.7)
Bottled drinking water 9	DBP	0.56	97.3 (1.8)	Barrelled drinking water 9	DBP	0.87	96.8 (3.0)
	DEHP	nd	92.6 (2.1)		DEHP	nd	93.6 (1.9)
Bottled drinking water 10	DBP	nd	98.0 (5.4)	Barrelled drinking water 10	DBP	nd	97.3 (2.4)
	DEHP	2.51	93.4 (3.7)		DEHP	2.01	93.5 (3.5)

[a] Mean for three determinations.

[b] Mean and RSD for three determinations; nd: not detected.

3.3 *Analysis of real samples*

On the basis of the experiments carried out in this study, CGFR was selected to pretreat the real samples. This method was used to analyse 10 bottled drinking water samples and 10 barreled drinking water samples available from the local market. The results are listed in Table 3. Recovery tests were carried out on water samples spiked with standard DBP and DEHP mixtures, and the results presented in Table 3. Among the 20 samples studied, DBP was found in 15 samples with concentration levels ranging from $0.52\,\mu g\,L^{-1}$ to $56.1\,\mu g\,L^{-1}$, while DEHP was found in 14 of the 20 samples ranging from $1.93\,\mu g\,L^{-1}$ to $3.66\,\mu g\,L^{-1}$. It can be seen from Table 3 that the observed residues of the DBP and DEHP were considerable.

4. Conclusion

In this paper, the absorbent effect of MWCNTs, CGFR, and C_{18} for DBP and DEHP analysis was compared, and HPLC was used to analyse the DBP and DEHP absorbed by the three solid-phase extraction materials. The recoveries, and linear ranges of the SPEs using CGFR and MWCNTs were compared with those obtained using conventional C_{18} SPE adsorbents, and the results indicated that CGFR for its high recovery was more effective than, or as effective as the C_{18} adsorbents, for the solid-phase extraction of DBP and DEHP in drinking water. However, the recoveries of MWCNTs ranging from 59.7% to 63.0% used in our test for DBP and DEHP did not satisfy the request of the experiment. From the foregoing, it was found that CGFR possesses a remarkable potential for use in the solid-phase extraction of trace DBP and DEHP from drinking water. The results demonstrate that the proposed method is simple, rapid, and reliable for routine analysis of DBP and DEHP.

Acknowledgements

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