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Application of modified nano γ-alumina as a solid-phase extraction sorbent combined with high-performance liquid chromatography for determination of phthalate esters in environmental water and soft drink samples

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ABSTRACT

A solid-phase extraction procedure based on sodium dodecyl sulfate (SDS)-coated nano γ-alumina was used for the first time as an effective adsorbent for preconcentration of four phthalate esters in environmental water and soft drink samples for their subsequent determination by high-performance liquid chromatography with ultraviolet detection. The system of anionic surfactant SDS with hemimicelles/admicelles formed on the oxide mineral surface was used. Properties of the nano γ-alumina were characterized by field-emission scanning electron microscopy. Several predominant factors affecting the adsorption of phthalate esters were optimized. Under the optimized conditions, preconcentration of 500 mL of the sample solution permitted a preconcentration factor of 500 for all analytes. The linear response was achieved in the concentration range of 0.1–200 μg L^{-1}. Limits of detection of the method obtained at a signal-to-noise ratio of three ranged between 0.042 and 0.060 μg L^{-1}. The Langmuir adsorption capacity (q_{max}) was found to be in the range of 66.7–83.3 mg g^{-1} of the adsorbent. The method was successfully applied for the determination of phthalate esters in different samples with good recoveries ranging from 94.0 to 106.0% with relative standard deviation values below 6%.

Keywords: Phthalate esters; Nano γ-alumina; High-performance liquid chromatography; Hemimicelles/admicelles

1. Introduction

Phthalate esters (phthalic acid esters, PAEs) are famous polymer additives, used primarily as plasticizers to soften polymeric materials like polyvinyl chloride and improve some other of their mechanical properties. Further, they are used in production of pesticides, paints, etc. In spite of the use of phthalates in a large variety of products, in recent years [1], these compounds have been omitted from plastics either because there is no covalent bond between the phthalates and plastics in which they are combined, and are therefore free to migrate, or because during the use of the plastic product, the plastic becomes distorted, worn,

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or weathered. This can lead to the exposure and loss of previously bound compounds. Exposure to sunlight (especially UVB) can degrade plastics. Many of the chemicals in use have not been subjected to a risk assessment [2]. Certain PAEs compounds and/or their metabolites have recently been implicated in having adverse effects on human health, specifically on the liver, kidney, and testicles [3–5]. Due to the trace concentration level of PAEs and interference of the complicated matrix, it is required to carry out sample preconcentration for an accurate determination of these compounds [5]. Therefore, considerable interest has been raised in the development of sample preparation for their determination in the water samples [6]. For this purpose, various analytical methods have been reported for determining PAEs by gas chromatography (GC) [7,8], high performance liquid chromatography (HPLC) [9,10], using different preconcentration methods such as liquid–liquid extraction (LLE) [11], solid-phase microextraction [12,13] and solid-phase extraction (SPE) [14–17] in different matrices. Among the above-referred methods, SPE with different sorbents [5,14,15,18–20] was widely used. The micro-sized sorbents may cause low extraction efficiency especially in the determination of ultra trace analytes and a long time is required for passing the sample solution through the SPE column [21]. Recently, nanometer-sized materials have gained more attention due to their special properties [22]. Instead of micro-sized sorbents, nano-sized sorbents have a completely good adsorption performance [23]. Nowadays, nano-sized alumina exhibits extensive attentions due to high surface area, absence of internal diffusion resistance, high chemical activity, and surface binding energy [24,25] but is hydrophilic in nature, and shows limited adsorption capacities for hydrophobic compounds. It can be modified by the coating surfactant in term of hemimicelles/admicelles to enhance its adsorptive tendency towards organic compounds. In this paper, we intend to assess the use of modified nano alumina for the preconcentration of non-polar phthalate esters. After modification of nano alumina, the main experimental factors affecting on the adsorption and desorption were investigated and optimized. The research results provided an effective preconcentration and extraction PAEs in water and soft drink samples.

2. Materials and methods

2.1. Reagents and samples

The studied compounds diethyl phthalate (DEP), di-n-butyl phthalate (DBP), di-isobutyl phthalate (DIBP), and di-2-ethylhexyl (DEHP) phthalate esters were of analytical grade, obtained from Merck (Darmstadt, Germany). The stock standard solutions of 1000.0 mg L^{-1} of each PAE were prepared in methanol. The aqueous solutions were prepared by daily dilution of the working solution with ultrapure water. Standard solutions of analytes were stored at 4°C in the refrigerator. A Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for preparation of reagent water.

Nano γ–alumina surface (Al_2O_3-gamma powder, 40–80 nm, purity: >99%, NanoAmor, Los Alamos, New Mexico, USA) was activated by its shaking with 5 mol L^{-1} nitric acid and further washed three times with distilled water.

2.2. Instrumentation

Separation and determination of PAEs were performed on a 1100 Series HPLC instrument from Agilent Technologies (Waldbronn, Germany), equipped with a quaternary pump, a vacuum degasser, column compartments, and an UV/vis detector. The injection volume was set to 20 μL. The obtained HPLC data were processed by Agilent Chemstation software. All data were evaluated using Microsoft Excel. The chromatographic separation was carried out by a reverse phase HPLC system, using an Eclipse XDB-C_{18} column (150 mm × 4.6 mm × 5 μm particle size) from Agilent Technologies. These four phthalate esters were chromatographically separated by using an isocratic mobile phase of methanol–water of 70:30 v/v. The flow rate and detection wavelength were 1.0 mL min^{-1} and 230 nm, respectively.

Field-emission scanning electron microscopy (FESEM, Hitachi, S-4,160, Japan) was used for preparation of SEM images.

2.3. Preparation of modified nano γ-alumina

1 g of activated nano γ-alumina was suspended in a 50 mL water solution containing 100 mg of sodium dodecyl sulfate (SDS) in a 100 mL flask, the pH of solution was adjusted to 2–2.5 and the flask was mechanically shaken for 15 min. Further, the mixture was filtered and washed with highly pure-deionized water, and 50 mg of this sorbent was stored to be used for further experiments. Fig. 1(a) and (b) shows the SEM image of Fig. 1(a) and (b) shows the FESEM image of naked nano γ-alumina and modified SDS nano γ-alumina . The naked alumina nanoparticles had a mean diameter of 53 nm. After modification process, the modified nanoparticles prepared are in the range of 75 nm in diameter. As shown in Fig. 1(b),

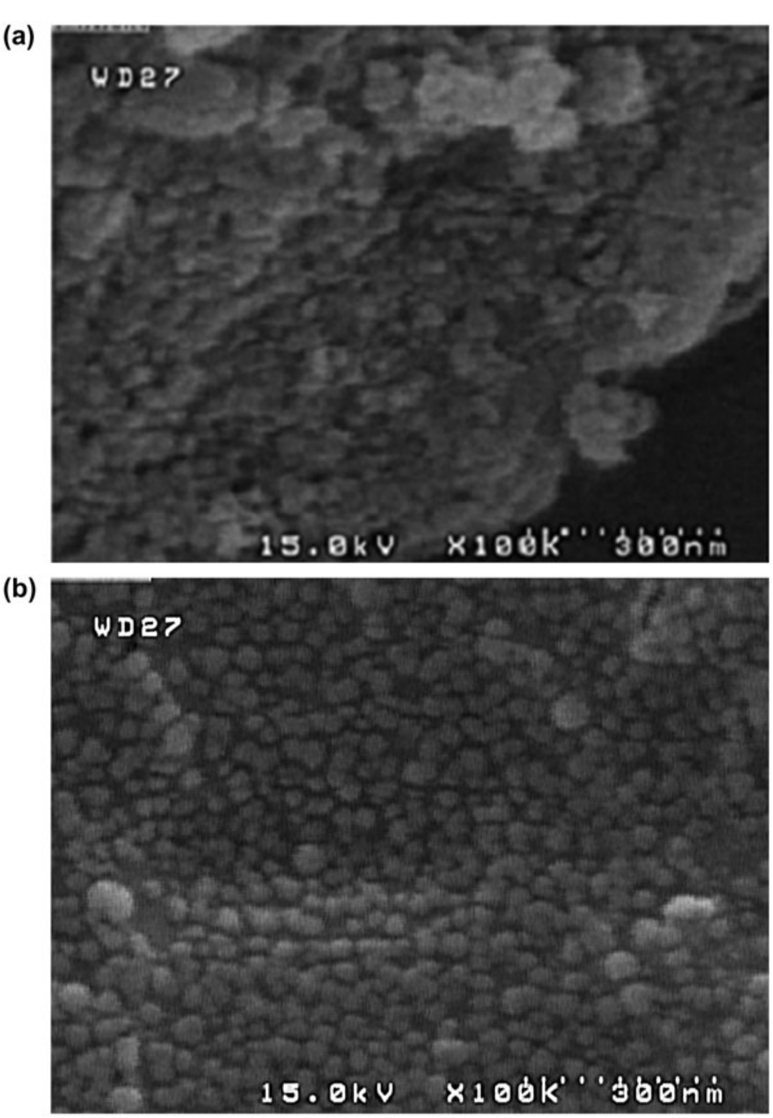

Fig. 1. The FESEM image of naked nano γ-alumina (a) and modified SDS nano γ-alumina (b).

after the modification process, the modified nano alumina became enlarged in diameter in comparison with a naked nano alumina. This showed that the nano alumina had been completely coated by the SDS. There are some agglomerations in the nanoparticles before modification, but this problem has resolved after modification the nanoparticles.

2.4. Sample preparation

Several samples, including tap water, sea water, bottled mineral water, water exposed to polyethylene container, and soft drink (beverage) sample were studied. Tap water sample was freshly collected from our laboratory (University of Tehran, Iran), sea water from the Caspian Sea (Iran), and bottled mineral water (Damavand mineral water, Iran) was purchased from local supermarkets in Tehran. The polyethylene containers were punched over a 3 cm diameter, agitated in 50 mL of water sample for 10 days.

Prior to their analysis, sea water samples were filtered through a 0.45 μm membrane to remove particles. Water samples were stored in glass bottles and kept in darkness at 4˚C.

2.5. Extraction and desorption procedure

The general procedure for extraction of phthalate esters was as follows: an aliquot of 50 mL of the sample solution containing four phthalate esters and

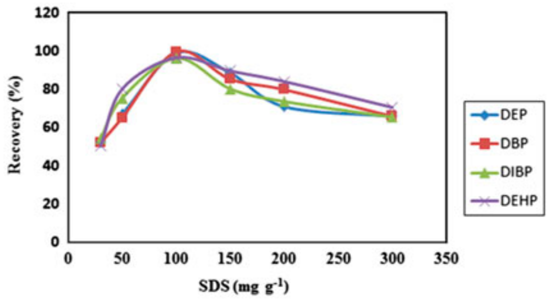

Fig. 2. Effect of amount of SDS on the extraction efficiency for phthalate esters, pH: 3, concentrations: 1 μg L^{-1}.

50 mg of modified nano alumina was put in a test tube. 0.1 mol L^{-1} solutions of HCl and NaOH were used to adjust the pH value to three. After shaking the mixture for about 1 min, the test tubes were placed in a centrifuge and centrifuged for 2 min at 5,000 rpm to accelerate the separation of the sorbent. Subsequently, the aqueous phase was easily separated by decantation. Analytes were then desorbed by addition of 2.0 mL of methanol to the sorbent. Finally, after shaking, the mixture was centrifuged (2 min at 5,000 rpm) to separate the sorbent. The eluent was dried with a stream of nitrogen, redissolved in 1 mL of methanol, and then later analyzed by HPLC with an injection of 20 μL.

3. Results and discussion

Solid-phase extraction of PAEs with modified nano alumina and unmodified nano alumina was studied. It was observed that the modified nano alumina gave a quantitative enrichment, while the unmodified alumina a recovery of ~8%.

The enrichment factor (EF) was defined as the ratio of the analyte concentration in the eluent (C_e) and the initial concentration of the analyte (c_i) in the sample based on Eq. (1):

$$EF = \frac{C_e}{C_i} \tag{1}$$

The extraction recovery was calculated as the percentage of the total amount of the analyte (m), which was extracted into the eluent

Where m_e *and* m_s are the amount of the analyte in eluent, and the amount of analyte in the sample, respectively.

$$R(\%) = \left(\frac{m_e}{m_s}\right) \times 100 = \left(\frac{C_e V_e}{C_i V_i}\right) \times 100 \tag{2}$$

3.1. The ratio of SDS to the sorbent

Fig. 2 shows the influence of the amount of SDS on the extraction efficiency of phthalate esters, based on the varying amount of SDS in the range of 30–200 mg g^{-1}. It was observed that phthalate esters could not adsorb on nano alumina, while with higher amounts of SDS the adsorption amounts efficiently increased. This increased adsorption can be caused by an occurrence of mixed hemimicelles (hemimicelles and admicelles) that are gradually formed on the nano alumina surface [26]. Further, it could be seen that the recovery of target analytes was enhanced by increasing the amount of SDS up to 100 mg g^{-1} nano alumina and then decreased. It can be suggested that with higher amounts of SDS, micelles begin to be formed in the sample solution and the micelles cause distribution of phthalate esters into the bulk solution [26]. In order to achieve high capacity and maximum adsorption in the following experiments, 100 mg g^{-1} of SDS was selected.

3.2. Effect of pH

The solution pH has a principle role in the adsorption amount of mixed hemimicelles system. The pH effect was studied in the range of 2–8. As the pH increases, especially above point of zero charge (PZC) of the alumina (about 8.5), a decrease in the amount of adsorption occur. This phenomenon can be considered as a proof that the nano alumina surface is positively charged at a pH lower than the PZC value. Therefore, the anionic surfactant SDS molecules are easily adsorbed on the nano alumina surface by a strong electrostatic attraction [26]. As a result, phthalate esters are adsorbed by the mixed hemimi-

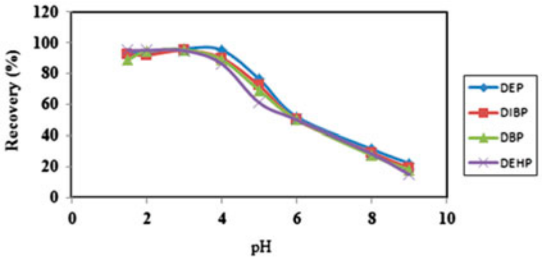

Fig. 3. Effect of pH on the adsorption of phthalate esters on modified nano alumina, concentrations: 1 μg L^{-1}.

celles through hydrophobic actions. Consequently, the highest retention for all analytes occurred at pH 3 measured on SDS- nano alumina (Fig. 3).

3.3. Choice of eluent: type and volume

The desorption of phthalate esters from modified nano alumina was performed with different organic solvents such as acetonitrile, methanol, and acetone. The results showed that methanol was the most suitable eluent for the four analytes due to a higher recovery and a complete elution of PAEs from modified nano alumina; therefore, it was chosen as the eluent. Also, effect of desorption time on the recovery of PAEs was investigated. Results showed that the extraction recovery increased by increasing the extraction time up to 0.5 min and after that remained constant. Thus, 0.5 min was used for the extraction time in the subsequent experiments.

Furthermore, the effect of the volume of methanol to elute all the four analytes from modified nano alumina was tested up to 5 mL with 50 mL of 1 μg L^{-1} standard solutions of all the four analytes. Quantitative recoveries (above 95%) were obtained in the range of 1–5 mL. Thus, 2 mL of methanol was accepted as the optimum volume of the eluent to desorb the components.

3.4. Effect of the amount of adsorbent

The amount of sorbent is another important parameter that affects the recovery. The effect of amount of modified nano alumina on the recovery of the four phthalate esters was examined by varying the amounts of the sorbent in the range of 5–300 mg. According to the obtained results, quantitative recoveries (>95%) of the PAEs were achieved when the sorbent quantity was greater than 30 mg. Hence, 50 mg of the modified nano alumina was used under the optimum conditions due to an increase in the surface area and available sites at high amounts of the sorbent.

3.5. Effect of the solution volume on SPE

The effect of the sample volume on the preconcentration factor of the analytes is important. For this reason, various volumes of the sample in the range of 10–1,000 mL were spiked with each analyte (0.05 μg) under the experimental conditions. As shown in Fig. 4, the obtained quantitative recoveries of the analytes were >95% up to 500 mL. Therefore, 500 mL sample volume was chosen. By concentrating the eluents (2 mL of methanol) to 1 mL with nitrogen flow, we could easily achieve concentration factors of 500 which showed the high extraction efficiency of the modified nano alumina sorbent.

3.6. Effect of ionic strength

To investigate influence of salt addition on the extraction efficiency of PAEs, various experiments were performed with different amounts of NaCl (0–10% (w/v)), while other experimental conditions were kept constant. Results showed that no significant variation in the extraction efficiency was observed with the NaCl concentration. Therefore, all the extraction experiments were carried out without the addition of salt.

3.7. Adsorption isotherm

The adsorption data were studied with the use of the Langmuir isotherm. The Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of homogeneous sites. It can be represented by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_{\text{ads}}} \tag{3}$$

where $q_{\max}$ is the maximum amount of PAEs adsorbed per unit weight of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of PAEs, q_e is the amount of

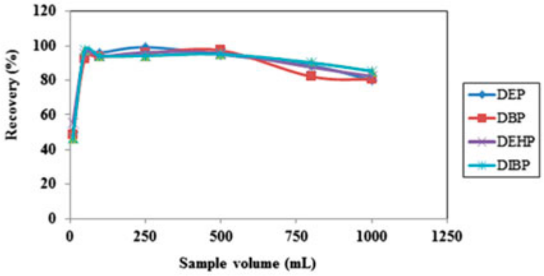

Fig. 4. Effect of sample volume on the recovery for phthalate esters, pH: 3, concentrations: 1 μg L^{-1}.

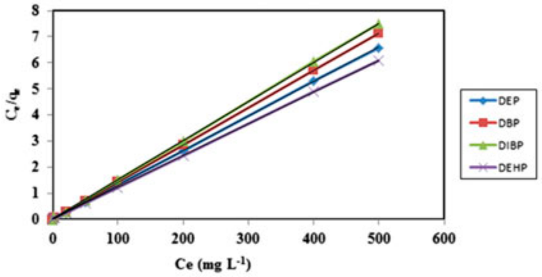

Fig. 5. Langmuir adsorption isotherm of PAEs for modified nano alumina.

Table 1
Parameters of Langmuir isotherm equations, regression coefficients (r) for the adsorption of PAEs on modified nano alumina at 25˚C and at pH 3.0

Analytes	$q_{\max}$ (mg g^{-1})	K_{ads} (L mg^{-1})	r
DEP	76.9	1.18	0.9997
DEHP	83.3	0.60	0.9998
DBP	71.4	1.16	0.9996
DIBP	66.7	0.83	0.9997

Table 2
Analytical parameters of the proposed method

Compound	LOD (μg/L)	Linear range (μg/L)	R^2	RSD ($n = 10$)[a] (%)
DEP	0.042	0.1–200	0.9985	4.5
DBP	0.060	0.1–200	0.9940	5.7
DIBP	0.053	0.1–200	0.9945	5.8
DEHP	0.055	0.1–200	0.9996	5.3

[a] Concentration was 1 μgL^{-1} for which RSD was obtained.

PAEs adsorbed per unit weight of adsorbent at equilibrium concentration (mg g^{-1}), and K_{ads} is the Langmuir constant related to the affinity of binding sites (L mg^{-1}) (Fig. 5). Values of $q_{\max}$ and K_{ads} are determined from the linear regression plot of (C_e/q_e) vs. C_e. The calculated parameters and the correlation coefficients (r) are listed in Table 1. The plot of (C_e/q_e) vs. C_e for each PAE gives a straight line with a correlation coefficient in the range of 0.9996–0.9998.

The equilibrium adsorption capacity of adsorbent (q_e, mg g^{-1}) was calculated according to the following equation:

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{4}$$

where C_0 is the initial concentration of the PAEs in mg L^{-1}, C_e is the equilibrium concentration in mg L^{-1}, V is the volume of the sample solution in L, and w is the weight of the nano alumina in g. According to the obtained results, the maximum amount of PAEs sorbed by modified nano alumina was in the range of 66.6–83.3 mg g^{-1}.

3.8. Analytical performance

To present the feasibility of the proposed method, analytical quality parameters were also investigated, including linearity, repeatability, and limit of detection. Table 2 shows the analytical characteristics of the

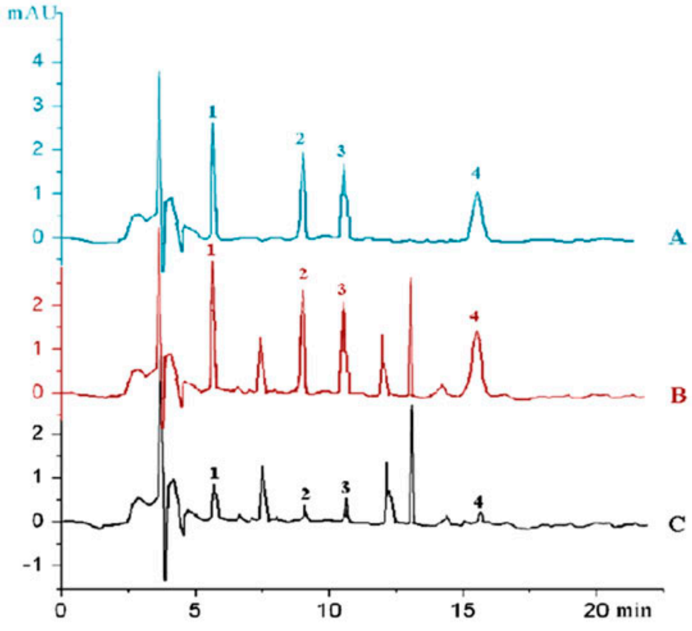

Fig. 6. The typical chromatograms extracted with modified nano alumina. (A) tap water sample spiked with 10 μg L^{-1} of each analyte. (B) sea water sample spiked with 10 μg L^{-1} of each analyte, and (C) non-spike sea water sample. Peak: (1) DEP, (2) DIBP, (3) DBP, and (4) DEHP.

Table 3
Determination of phthalate esters in real water and spiked water samples

Analyte	Tap water[a]			Beverage (soft drink)			Botteled mineral water[d]			Water exposed to polyethylene container			Sea water[e]		
	Spiked (μg/L)	Detected (μg/L)	RR (%)[b,c]	Spiked (μg/L)	Detected (μg/L)	RR (%)	Spiked (μg/L)	Detected (μg/L)	RR (%)	Spiked (μg/L)	Detected (μg/L)	RR (%)	Spiked (μg/L)	Detected (μg/L)	RR (%)
DEP	1	0.97 ± 0.05	97	1	1.0± 0.05	96	1	1.09±0.06	96	1	1.07±0.05	96	1	1.75±0.07	95
	10	9.4 ± 0.4	94	10	9.8± 0.4	98	10	10.11±0.4	98	10	10.08±0.4	98	10	10.71±0.5	90
DBP	1	0.95 ± 0.06	95	1	1.10±0.06	95	1	1.13±0.06	95	1	1.18±0.07	95	1	1.68±0.09	95
	10	9.6 ± 0.6	96	10	9.90±0.5	96	10	10.12±0.6	96	10	10.19±0.6	96	10	10.72±0.6	106
DIBP 1		0.96 ± 0.06	96	1	0.98±0.06	96	1	1.05±0.06	96	1	1.07±0.06	96	1	1.36±0.08	96
	10	9.5 ± 0.6	95	10	9.6±0.6	95	10	10.05±0.6	95	10	10.06±0.5	95	10	10.34±0.6	95
DIBP	1	0.96 ± 0.05	96	1	0.97±0.06	97	1	1.09±0.06	97	1	1.11±0.06	97	1	1.19±0.06	98
	10	9.7±0.5	97	10	9.9±0.6	95	10	10.08±0.6	95	10	10.14±0.6	95	10	10.16±0.6	96

[a] Tehran city.

[b] Relative recovery.

[c] Mean and standard deviation for three determinations.

[d] Damavand mineral water, Iran.

[e] Caspian Sea (Iran).

Table 4
Comparison of the proposed method with other methods reported

Sorbents	Technique	Analyets	LOD (μg/L)	EF[a]	Volume sample (mL)	Sorbent amount (mg)	RSD (%)	Reference
RTILs-silica	HPLC-UV	DEP, DnPP, DnBP, DcHP, DEHP	0.12–0.17	600	300	15–30	≤6.0	[5]
Carbon nanotubes	HPLC-DAD	DEP, DnPP, DcHP, DIBP	0.18–0.86	200	1,000	500	–	[17]
polystyrene	LC-UV	BBP, DEHP	0.05–0.1	–	–	–	1.1–4.2	[19]
Florisil	GC-FID	DMP, DEP, DBP, DEHP	25–50	200	100	1,000	<3	[15]
Fe_3O_4@C_{18}@Ba^{2+}-ALG	HPLC-UV	DPP, DBP, DCP, DOP	0.019–0.059	500–1,000	500	100	1–9	[27]
Silica gel	HPLC	BBP, DBP, DCHP	3.1–6.3	40–80	100–200	300	–	[14]
Modified nano alumina	HPLC-UV	DEP, DBP, DIBP, DEHP	0.042–0.060	500	500	50	<6	This work

[a] Enrichment factor.

Table 5
Comparison of proposed method with other methods based on preparation and extraction time

Methods	Solid phase preparation time	Reagent	Total extraction time (min)	Reference
SPE-HPLC/UV	>12 h	Fe_3O_4–C_{18} MNPs[a]	30	[21]
SPE-HPLC/UV	>12 h	Barium alginate caged Fe_3O_4@C_{18} magnetic	30	[27]
SPE-HPLC-/PDA	>48 h	CTAB[b]	–	[28]
MSPE-GC/MS	>6 h	Fe_3O_4	5	[29]
Micro SPE-GC/MS	>24 h	Fe_3O_4@mSiO_2 and CTAB	20	[30]
SPE-HPLC/UV	15 min	SDS	10	This work

[a] Magnetite nanoparticles.
[b] Cetyltrimethylammonium bromide.

method. A good correlation coefficient was obtained. The calibration curves were linear up to 200 μg L^{-1}. The limits of detection (LODs), based on the signal-to-noise ratio (S/N) of three, ranged from 0.042–0.060 μgL^{-1}. Relative standard deviation (RSD) for 10 replicate measurements of 1 μgL^{-1} phthalate esters was <6%. Therefore, the proposed method can be considered as a sensitive and repeatable method with high enrichment factors for the preconcentration of PAEs at trace levels.

3.9. Analysis of real water samples

The proposed method was applied to determine phthalate esters in different water and soft drink samples. The water samples were analyzed by SPE as a prior step to their enhanced determination by HPLC. The samples were spiked with variable amounts of PAEs to assess matrix effects. Fig. 6 presents typical chromatograms of the extracted phthalate esters from non-spiked sea water sample, and from tap and sea water samples spiked with 10 μg L^{-1} of each analyte. Table 3 shows the analytical results of the real samples obtained after three replicate extractions of each sample. It can be observed that the recoveries for the spiked real samples ranged from 94 to 106%.

3.10. Comparison of analytical characteristics of the presented method with other SPE methods

In order to further present the superiority of the proposed method, it was compared with other SPE methods with different adsorbents reported in the literature. As listed in Table 4, LODs and RSDs of the proposed method prove to be significant when compared with other methods, thus indicating a highly sensitive detection of PAEs with the modified nano alumina high-performance liquid chromatography with ultraviolet (HPLC-UV) method. Also, this method offers advantages of a simpler preparation procedure and a smaller required adsorbent amount. Moreover, the proposed method was compared with other methods regarding preparation and extraction time and as seen in Table 5, both the procedures were performed in a short time.

4. Conclusions

In this study, a SPE procedure based on modified nano alumina as sorbent, combined with HPLC-UV was performed for determination and preconcentration of four phthalate esters in water and soft drink samples. Preconcentration was based on the formation of hemimicelles/admicelles on the nano alumina surface. The maximum adsorption of phthalate esters was observed at pH 3 and the recovery was >95% in the range of 0.1–200 μg L^{-1}. The analytical data demonstrate accuracy and precision of the applied method, which can meet requirements for analysis of biological samples. Also this analytical technique proposes numerous advantages, such as ease of operation, availability of reagent, short extraction time, and high enrichment factors. In addition, the combination of mixed hemimicelles and nanoparticles provides an easy elution and only a small volume of the eluent, therefore being an environmentally friendly approach. The results showed that this method was effective for the preconcentration of trace phthalate esters in different samples.

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