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Application of Polyethylene Glycol Grafted-CuO Nanoparticles in Solid Phase Extraction of Phthalate Esters in Baby Shampoo and Body Wash

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Abstract
This study considers identification and determination of phthalates esters in cosmetic samples. The dispersive solid phase extraction was used for extraction of analytes prior to high performance liquid chromatography analysis. The solid sorbent for extraction was polyethylene glycol grafted on cupric oxide nanoparticles (PEG-g-CuO-NPs). This sorbent was first synthesized and characterized by scanning electron microscopy (SEM), Energy-dispersive X-ray (EDX) and fourier-transform infrared spectroscopy (FT-IR) then efficiently applied for extraction of analytes. The extraction conditions like amount of sorbent, kind and volume of desorption solvent, extraction and desorption time, and pH of sample solution were optimized. The validation of method carried out under optimum conditions. Linear ranges were 0.005-4 μgmL^{-1} with the coefficient correlation (R^2) in the range of 0.9914-0.9962. The limits of detection (LODs) (3S/N) were 0.0025 to 0.005 μgmL^{-1} and acceptable repeatability's (RSDs below 6.45%, n=5) obtained. Application of proposed method was investigated by extraction of phthalates in shampoo and body wash for babies which satisfaction results achieved.

Keywords: Phthalate Esters; HPLC; Baby Shampoo; Body Wash; Polyethylene Glycol Grafted Cupric Oxide Nano Particles.

1. INTRODUCTION

Phthalates or phthalate esters are esters of phthalic acid. They are used in large variety of products [1]. They are mainly used as a plasticizer in order to improve flexibility, transparency, durability, and longevity of plastics specially polyvinylchloride (PVC). Phthalates also used in making wide variety products such as pharmaceutical pills, gelling agents, building materials, personal-care products, medical devices, food package, toys, detergents and so on [2-5].

Almost all cosmetics contain phthalates, they appear in cosmetics in two forms, ingredient or harmful material. They may be used as solvents for fragrances to raise scent durability or likely used as a gelling agent and fragrance aid in the shampoo or moisturizer in body shampoo or in other place used as anti-cracking in nail polishes, and as a softener in hand cream [6, 7]. However, manufactures of cosmetic products are not in forced to reveal the ingredient in consumer product labels. For example, a typical fragrance may contain several type of phthalates which are often hidden [8]. Despite the extensive use of phthalates, its destructive effects are not considered. Phthalates can damage the liver (obesity and type II diabetes) [9-11], kidneys (kidney cancer) [12], lungs (asthma) [13, 14], and reproductive system (male genital birth defects and male fertility) [15, 16]. Therefore, the investigation the presence of the phthalates and in the next step measurement of these analytes will be important. Of course, extraction of analytes from the samples before presentation to instrument is inevitable. Until now, different extraction methods, liquid or solid phase, were applied for extraction of phthalates [6, 17-21].

Regarding the disadvantages such as the time consuming, using toxic organic solvents, environmental contamination, and fewer number of organic solvents and therefore less selectivity, liquid phase extraction is less popular than the solid phase extraction [22, 23]. The most important advantage of solid phase extraction is the possibility of making absorbent proportional to the analyte, or, in other words, selective adsorbent. For separation and identification of phthalates both instruments; HPLC (high performance liquid chromatography) [24-26] and GC (gas chromatography) were used. [27, 28].

Most of the methods used GC-MS for the detection and quantification of the phthalates, because it is a common method with high sensitivity and precision.

In this research, polyethylene glycol grafted flower-like cupric nano oxide (PEG-PEG grafted CuO-NPs) was used as sorbent for dispersive

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solid phase extraction (d-SPE) of phthalates. This sorbent based on copper oxide nanoparticles (flower-like) coated with a polymer of polyethylene glycol [29]. Until now, nanoparticles of copper were used for absorption of phthalates [30, 31]. on the other hand, hydrocarbon chains of polyethylene glycol on sorbent by π-π interaction with aromatic rings of phthalates could help to improve extraction efficiency of phthalates.

The objective of this research is to consider the application of PEG-PEG grafted CuO-NPs as a sorbent in dispersive solid phase extraction of phthalates and then separation and identification of analytes by HPLC-diode array detection (HPLC-DAD) and eventually the method evaluated for extraction and determination of phthalates in shampoo and body wash for babies as real samples.

2. EXPERIMENTAL

2.2.Chemicals, materials and samples

Poly (ethylene glycol) (PEG, MW 6000), sodium chloride, copper (II) nitrate ($Cu(NO_3)_2$), HPLC-grade methanol and acetonitrile, Ethanol, 2-propanol, hydrochloric acid (37%), sodium hydroxide (NaOH) were obtained from Merck (Darmstadt, Germany). Ammonium bicarbonate (NH_4HCO_3) from SIGMA-ALDRICH St. Louis, Missouri, United States.

Dimethyl phthalate (DMP), di*n*-butyl phthalate (DBP), benzyl butyl phthalate (BBP), hexane were purchased from Aldrich. Sodium chloride were supplied by Riedel-de-Haën.

Shampoo and body wash for babies were selected from popular brands used and existed in retail markets in the country.

2.2. Preparation of standard solutions

Mixed stock solution at concentration 2000 mg L^{-1} of DMP, DEP, DBP, BBP were prepared by dissolving the pure phthalate esters in acetonitrile and stored in 4 ^{0}C. Also, preparation of working standard solutions were performed by dilution appropriate amount of the stock solution with distilled water (0.1 µgmL^{-1}). The pH of aqueous solutions was justified by hydrochloric acid or sodium hydroxide.

2.3. Apparatus

Separation and determination of phthalates was performed by HPLC-DAD. The HPLC system consisted of Agilent 1260 (Santa Clara, CA 95051. United States*)*, Agilent 1260 Infinity Bio-inert Quaternary Pump, Agilent 1260 Infinity Bio-inert Manual Injector valve equipped with a 20 µL sample loop, a vacuum degasser, and a column compartment, coupled to a DAD, A Zorbax Eclipse XDB C18 column, 150 mm × 4.6 mm, 5 µm, at an oven temperature of 30 ^{0}C was used for separation, Agilent 1260 Infinity Diode Array Detectors DAD and Agilent ChemStation software. The degassed mobile phase was a mixture of acetonitrile-pure water (85:15%, v/v) and the flow rate was 1 mL min^{-1}. The analytes were detected by DAD at wavelength, 224 nm.

Centrifugation of solutions were carried out in Sigma 3-30KS centrifuge high speed (Osterode am Harz, Germany).

The characterization of the synthesized composite was performed by following instruments: surface properties of prepared were characterized by SEM (LEO, VP 1450, Zeiss, Wetzlar, Germany) equipped with EDX for elemental analysis (software IDFix, the beam: accelerating voltage: 15 kV, beam current: 700 nA), FT-IR spectra were recorded on the Thermo-Nicolet AVATAR 370 FT-IR w/SMART Endurance ATR spectrometer (Thermo Fisher Nicolet, USA) in the range of 400–4000 cm^{-1} in spectral-grade KBr pellets.

2.4. Preparation of baby shampoo for extraction

0.1 g of shampoo was weighted in vial then, after adjusted the pH to 6 the volume of solution was set at 20 mL with doble distilled water.

2.5. Preparation of baby's body wash for extraction

0.2 g baby's body wash was mixed with 1 mL ethanol; pH of solution was adjusted to 6 and then diluted to volume of 20 mL with double distilled water (Gimeno et al. 2012) before performing dispersive solid phase extraction.

2.6. Synthesis of Polyethylene glyco grafted CuO nanoparticles

The nanoparticles synthesized based hydro-thermal method according to previous research [32]. Briefly, aqueous solutions of $Cu(NO_3)_2{\cdot}3H_2O$ (25 mL) and NH_4HCO_3 solution (2.0 mol L^{-1}) (30 mL)were mixed with vigorous stirring, a blue precipitate was produced. After filtering the precipitate, 80 mL PEG solution (5 % wt.) was added, the mixture was placed in a stainless autoclave, heated at 170 ◦C for 24 h, after cooling, the produced black nanocomposite washed by ethanol-water for several times to remove any redundant reagent, and finally dried at 60 ℃ overnight.

2.7. Characterization and chemical composition of PEG-g-CuO-NPs

FT-IR spectrum of CuO nanparticles was shown in Fig. 1(a). In this figure can be found the peaks at 431.93 cm^{-1}, 498.07 cm^{-1}, 528.06 cm^{-1}, 603.10 cm^{-1} for existence of Cu-O bond stretching and bending vibrations [33]. After grafting

polyethylene glycol on nanoparticles (Fig.1(b)) the band appeared in spectrum; 2872.12 cm^{-1} due to existence of C-H group vibration, band at 3412 cm^{-1} correspond to O-H stretching vibration and CH group presented bands in 1066 cm^{-1} and 1029 cm^{-1} [34].

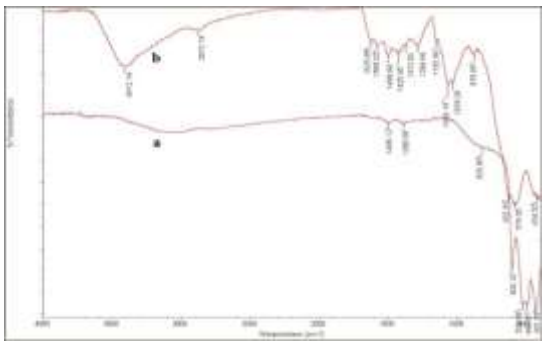

Fig. 1 The FT-IR spectra of the CuO nanoparticles (a) and PEG-g-CuO (b).

The morphology of surface carried out by scanning electron microscope (SEM) equipped with EDX analyser (Fig. 2). As can be seen, the flower-like uniform nano-sized CuO nanoparticles are shown. They have completely regular structure filled with fine particles On the other hand, the SEM image of PEG grafted CuO NPs showed associating of carbon chain on copper oxide nanoparticles. By adding PEG on the surface, the adsorption capacity of the species enhances and helps to improve the extraction efficiency. In this way grafting polymers of polyethylene glycol was confirmed.

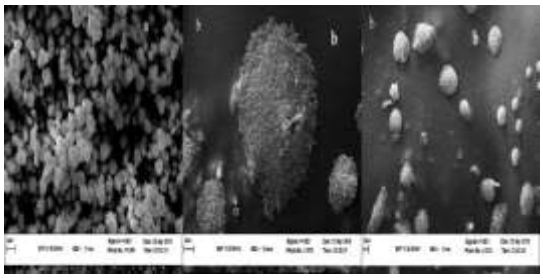

Fig. 2 SEM images of CuO nanoparticles (a) and PEG-g-CuO (b, c).

The SEM estimations specify that the flower-like CuO products were collected of microspheres with diameters of 0.8–1.2 μm. The microspheres were assembled from small needle-like nanocrystals with diameters of 20-25 nm. The diameter of PEG-g- CuO microspheres were 2.5-4.0 μm.

Chemical composition of these two materials (CuO nanoparticles and PEG-g-CuO-NPs) was investigated by elemental analysis (EDS) in Fig. 3. The peaks correspond to Cu, O and C after grafting PEG on CuO NPs can be seen.

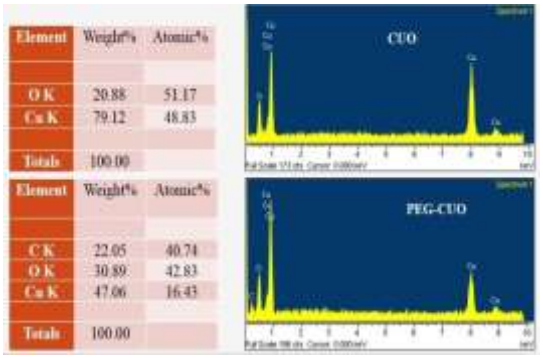

Fig. 3 Energy-dispersive X-ray (EDX) spectrum of CuO and PEG-g-CuO.

2.8. Dispersive solid phase extraction procedure

20 mL of sample aqueous solution (pH 4) containing analytes in vial was mixed with 40 mg solid sorbent. The mixture was vigorously stirring on magnetic stirrer for 15 min, phthalates were adsorbed on the surface of the nanocomposite. In the next step, for desorption of analytes, the mixture was centrifuged at 6000 rpm for 10 min for isolation of sorbent, the supernatant decanted and 100 μL acetonitrile was added to the nanoparticles enriched with analytes, stirring for 4 min and finally 10 μL of acetonitrile (after centrifugation) injected to HPLC for further analysis.

2.9. Optimization of d-SPE procedure

Factors affecting the extraction process were evaluated to find out the best extraction conditions. Effect of amount of solid sorbent, kind and volume of desorption sorbent, time of extraction, desorption time and pH of sample solution were investigated. For optimization process the concentration of analytes was 0.5 ppm, each experiment repeated 3 times, and to calculate the calibration curve each concentration level repeated 3 times and to calculating LOD each experiment repeated 5 times.

2.10. Kind of desorption solvent

Kind of desorption solvent should be consistent with the analytes, and it should simply desorb them. On the other hand, solvent should have appropriate polarity for desorbing of analytes.

For this purpose, five kind of solvents (acetonitrile, methanol, ethanol, 2- propanol, hexane) were considered (Fig. 4a). The acetonitrile showed a distinct strength in the desorption of analytes compared to other solvents. Acetonitrile is a polar aprotic solvent a medium-polarity solvent that is miscible with phthalates. This solvent also suitable for HPLC injection. The acetonitrile generally has a higher elution strength than considered solvents. Therefore, acetonitrile was chosen for this purpose.

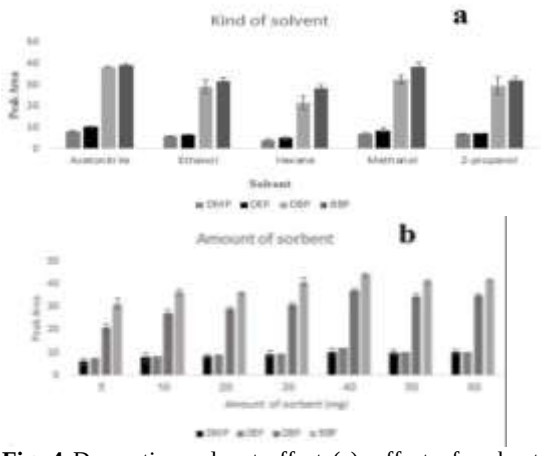

Fig. 4 Desorption solvent effect (a), effect of sorbent amount (b).

2.11. Effect of PEG-CuO NPs amount

NPs have effective surface, so that low amount of sorbent will be sufficient for extraction. On the other hands, synthesis of nanoparticles is time consuming.

Required amount of sorbent for extraction of analytes from 20 mL solution was considered in the range of 5 to 60 mg. As in Fig. 4b showed, the peak area increased with the addition of the amount of PEG-CuO NPs. With 40 mg sorbent provide the most extraction efficiency and selected for subsequent extraction. Performing the extraction can be easily done in amounts greater than 40 mg, but the peak areas will not be much different. In fact, the extraction efficiency is not much improved when amount of solid sorbent varied from 40 mg to 60 mg. We can say, the 40 mg sorbent will be sufficient for adsorbing and extracting the phthalates from 20 mL aqueous sample.

2.12. Extraction time effect

The time it takes to extract is very important. Extraction time was investigated in the range of 5 to 35 minutes. The peak areas were almost the same at all of these times, although it was 15 minutes, with slightly difference had the most peak areas than the others. The results were shown in Fig. 5a. If more time is allocated to extraction, it may desorb the analytes and decrease extraction efficiency. During the extraction time efficient adsorption should be carried out. By performing extraction in fifteen minutes the desired result will be provided.

2.13. Effect of desorption time

Desorption time was tested from 2 min to 14 min. Fig. 5b depicted the results. 4 min was the optimum desorption time for analytes. By taking 4 minutes to desorb the species, the analytes were appropriately separated from the sorbent and after injection to HPLC the high peak areas were obtained. Desorption of PAEs would achieve similar results over longer periods of time and the peak areas would remain almost constant.

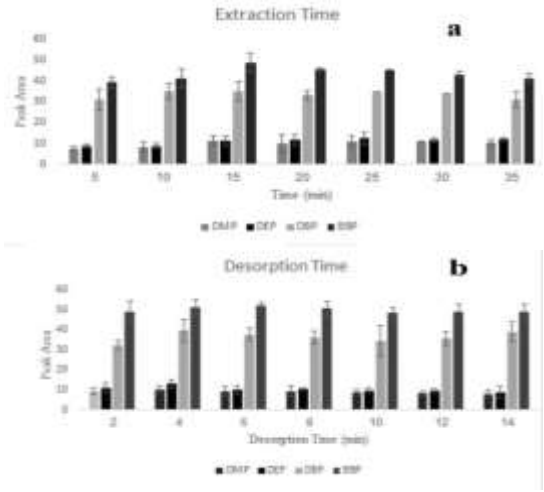

Fig. 5 Extraction time effect (a), desorption time effect (b).

2.14. Volume of desorption solvent

Volume of desorption solvent has impact on extraction efficiency. When finding the optimum volume, two issue should be considered; sufficient volume that can desorbed analytes from the solution and at the same time the preconcentration factor of extraction does not change. So that, the volume of acetonitrile was changed from 100 µL to 1500 µL. 100 µL provided the best extraction efficiency (Fig. 6a). 100 µL acetonitrile due to high elution power can desorb analytes from the surface of sorbent and no further amount of solvent was not required to apply.

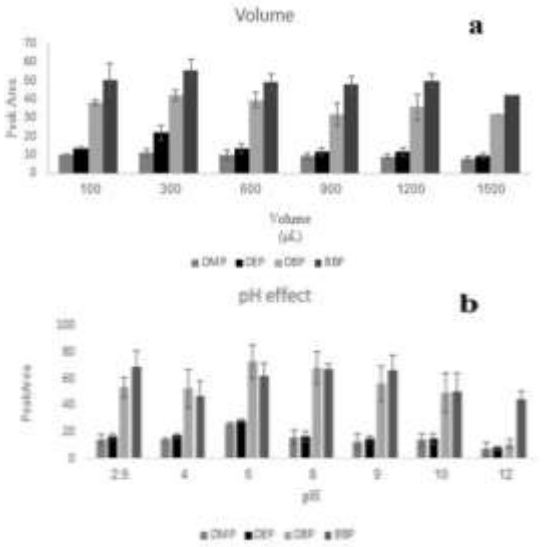

Fig. 6 Effect of desorption solvent volume (a) effect of sample pH (b).

2.15. Effect of sample pH

In dispersive solid phase extraction both analytes and kind of sorbent plays role in finding proper sample solution. The pH of sample was altered from 2-12 (acidic to basic) (Fig. 6b). Among them, by choosing pH on 6 the optimum results were obtained.

Phthalates are esters and chemical compounds, which include ester- can be decomposed in concentrated acids (low pH) or bases (high pH). Thus, the pH of sample does not have much effect on the extraction of these compounds, therefore in many studies on phthalates this factor has not been investigated.

However, in the case of a solid phase extraction, the sorbent type and the functional groups on solid sorbent effect on the extraction efficiency. Here, our sorbent was polyethylene glycol grafted- CuO, it means that, there are hydroxyl groups on the adsorbent surface structure that can interact with analyte and changes in the pH of the solution leads to variation of adsorbent surface charge. So, the semi-acidic or semi-alkalin condition would be suitable for extraction of analytes due to the hydrolysis reaction.

This phenomenon can be explained in another way; phthalate species are not hydrophobe in highly acidic or highly alkali environments, and it would not be in favor of extraction and the extraction efficiency will decrease. In extremely low pH, phthalates appear as phthalic acid with high polarity and at high pH, they will be hydrolysed to phthalate anions. So, when sample pH was 6 or 8, the extraction efficiency was maximum. The pH of natural solution of mixed phthalates is 6, so the pH of sample solution was set on 6.

2.16. Investigation of sorbent reusability

In order to find out the numbers of recoveries sorbent, 40 mg sorbent selected and extraction procedure carried out on them, after performing d-SPE , again aqueous solution added and the extraction done again. It was repeated for 10 times. The extraction resultants gathered and injected to HPLC. RSDs % of results calculated (9.04%) Therefore, we can conclude that the adsorbent can be used up to 10 times without changing the power. After performing 10 experiments by means of just 40 mg solid sorbent, the extraction efficiency decreased by more than 5% and the repeatability also decreased. Probably the reason could be that the sorbent amount during carrying out extraction by washing or the steps of adsorption and desorption was lost.

2.17. Analytical performance

Analytical performance features of the proposed method for phthalates were as follows. A series of phthalates standard calibration solutions were sampled to measure peak area according to the optimal experimental conditions. Limits of detection, linear range, precision (R.S.D.%) and repeatability were calculated and listed in Table 1. For conducting the calibration curve, 10 concentration levels for each analyte was considered. Each level was repeated three times. To calculate the detection limit, several aqueous solutions of analytes prepared, extraction procedure carried out on that solutions, the results of extraction injected to HPLC, where the peak heights of analytes are three times of the background (signal to noise=3), that concentration called limit of detection. Limit of quantification were obtained in same way just when signal to noise was 10.

2.18. Application of method to the real samples

Dispersive solid phase extraction was applied for extraction of phthalates in shampoo samples. Firstly, samples were prepared according to the description given in the the sample preparation section, then, analysis of real samples has been performed, as a first step. As shown, the results of the analyte identification in some samples are listed in Table 2.

Table 1. Figures of merit of the proposed method in determination of phthalate esters

Analytes	Retention time (min)	Linear range μgmL^{-1}	RSD% (n=5) Concentration Levels (μgmL^{-1}) 0.006 0.02 0.2	LOD μgmL^{-1}	LOQ μgmL^{-1}	EF	R^2
DMP	1.58	0.005-4	4.71 4.43 4.34	0.002 $\pm 5.21\times10^{-4}$	0.007 $\pm 4.38\times10^{-4}$	26	0.9945
DEP	1.95	0.005-4	3.54 1.22 5.28	0.002 $\pm 6.18\times10^{-4}$	0.007 $\pm 5.01\times10^{-4}$	38	0.9959
DBP	2.06	0.005-4	5.41 0.86 1.75	0.0025 $\pm 4.27\times10^{-4}$	0.0080 $\pm 6.33\times10^{-4}$	52	0.9962
BBP	2.21	0.005-4	6.45 2.67 2.17	0.0025 $\pm 3.31\times10^{-4}$	0.0080 $\pm 2.54\times10^{-4}$	48	0.9914

Table 2. Concentration of the studied PAEs in the baby's shampoo and body wash and their relative recoveries

Sample (0.1g)	DMP (µg+SD%)	*R.R%	DEP (µg+SD%)	R.R%	DBP (µg+SD%)	R.R%	BBP (µg+SD%)	R.R%
shampoo 1	4.00± 0.06	110.27	*NF	-	7.00± 0.09	86.09	2.00±0.02	93.21
Shampoo 2	0.80±0.02	97.52	NF	-	NF	-	NF	-
Shampoo 3	NF	-	NF	-	NF	-	2.40±0.06	101.11
Body wash 1	0.7±0.04	82.68	2±0.05	82.36	NF	-	NF	-
Body wash 2	NF	-	NF	-	4±0.05	87.41	NF	-

*R.R %: Relative recovery, *NF: Not found

Since the matrices of the real samples are complex, the standard addition method was used to identify the target analytes in the real samples. In the way that standard addition method was applied to the samples; different concentrations of phthalates were added to the same volumetric flasks which contain same amount of pretreated shampoo samples. The solutions were diluted to the mark. Then, after extraction the analytes by d-SPE, the extracted resultant injected into HPLC. The amount of phthalates in shampoo samples were determined by drawing the standard addition plots. The obtained results are presented in Table 2. The chromatograms of shampoo sample extraction before addition of standard solution (a) and after addition of standard (b) are shown in Fig. 7.

2.19. Comparison of this study with other similar reported methods for phthalates extraction

Table 3 was provided for comparison the results of the present study with the other extraction methods by emphasizing solid phase extraction of phthalates in different samples. PAEs can be found in almost all cosmetic and food samples in plastic container. By referring to this table, the detection limit of the methods with the mass spectrometer detector are much lower than other methods. This results reveal the high sensitivity of this detector. The same trend followed for the linear range. For cosmetic samples the analytical figures have the higher value than food samples, however in some studies LODs and/or RSDs were not calculated. The precision of this study was almost similar to other researches. The sensitivity of the method for investigating and measuring of phthalates in sanitary baby samples was adequate and appropriate. The results of this study were incoordinate with the results of the previous studies. See Table 3.

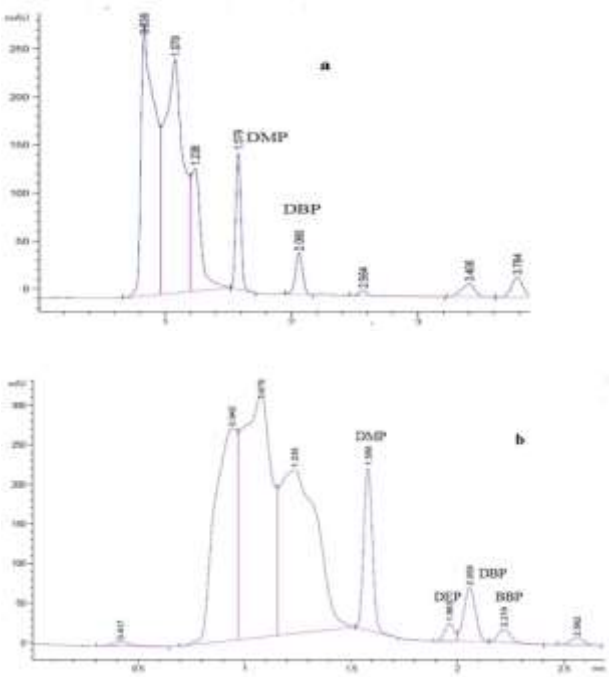

Fig. 7. Chromatogram of shampoo sample extraction, before addition of standard (a), after addition standard (b).

Table 3. Comparison this study with similar researches

Analytes	Real Sample	Extraction method (Instrument)	Linear Range ($\mu g mL^{-1}$)	LOD ($\mu g L^{-1}$)	RSD (%)	Ref.
DMP DEP BBP DBP DEHP	hair care products deodorants lotions creams nail products fragrances body washes	Solid phase extraction by Celite on disk (HPLC-UV)	1-1000	-	-	[35]
DBP BBP	Hand cream Lipstick	Solvent extraction,	100.00-5000	0.2 ng		[36]

DEHP DNOP DINP DIDP	Nail varnish Liquid Foundation Eye shadow	ultrasonic extraction and reflux (GC-MS)				
DMP DEP DBP BBP DEHP DOP	Body moisture gel Nailglass	Extracted with methanol by ultrasonic (GC-FID/GC-MS)	1–1000	0.1 ng	0.98 - 5.31%.	[37]
DEP DMP DiBP DnBP DEHP	Hair sprays Hair mousses Skin cleansers baby shampoos	solvent extraction (GC-MS)	-	-	-	[38]
DMP DEP BBP DBP DEHP	Antiperspirant Nail color Lotion Hair spray gel, mousse Deodorant Fragrance Body wash Shampoo Nail polish, color, enamel	Celite mixture with hexane (HPLC-UV)	-	LOQ 1-10 μg/g.	-	[39]
DEP DPP DAP DBP BBP DEHP	Water samples	Solid phase microextraction (SPME) GC-FID	0.001-0.1	0.032–0.451	Inter-batch 0.83–4.67% and intra-batch 3.08–9.73%	[40]
DiBP DnBP DMP DEP	Milk solutions and drinking water in baby bottle	Thin film microextraction-(TFME-GC-MS)	0.0005-0.25	0.1-0.15	<8.0%	[41]
DMP DEP BBP DBP DCHP	Beverages Plastic bottles	Magnetic dispersive solid-phase extraction (HPLC- UV)	beverages 0.0005-0.50 plastic bottles 0.05-50.00 μg g-1	beverages 0.09-0.28 and plastic bottles 0.01-0.03 μg g^{-1}	≤ 8.8%	[42]
DMP DEP BBP DBP	shampoo and body wash for babies	Solid phase extraction (HPLC-DAD)	0.005-4	2.5-5.0	<6.45%	This study

4. CONCLUSION

This study revealed that dispersive solid phase extraction and HPLC-DAD can be used for extraction and determination of phthalates in baby shampoo samples. PEG-g-CuO NPs was used as solid sorbent in d-SPE extraction. Shampoo matrixes are different with distilled water however, PEG-g-CuO had proper durability in these matrixes. The existence of hydroxyl groups on PEG could form hydrogen bonds with phthalates which improved adsorption of analytes to sorbent and proper extraction of them. This kind of sorbent was not applied for extraction of phthalates until now. Besides that, the sanitary samples (shampoo and body wash) for babies are not considered as yet despite the fact that they are very important.

Dispersive solid phase extraction as a new separation technique has expanded superior attention in the sample preparation procedure due to its simplicity, speed and high efficiency. Different kind of dispersion processes have been used within this technique to allow a close interaction between the sorbent and the aqueous sample solution during the trapping step, but also between the sorbent and the solvent in the

desorption step. This dispersion upgrades the kinetics of both sorption and desorption and so increases the efficiency of the overall extraction procedure. Extraction of phthalates in dispersive solid phase extraction was not carried out in these kind of samples and we have access to an efficient way to extract these materials. Therefore, it can be concluding this simple and rapid method could be easily used for extraction of phthalates in other cosmetic products.

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REFERENCES

[1] P.Gimeno, A.F. Maggio, C. Bousquet, A. Quoirez, C. Civade and P.A. Bonnet, Analytical method for the identification and assay of 12 phthalates in cosmetic products: Application of the ISO 12787 international standard "Cosmetics–Analytical methods–Validation criteria for analytical results using chromatographic techniques", *J. Chromatogr. A.* 1253 (2012) 144-53.

[2] J.C. Hubinger and D.C. Havery, Analysis of consumer cosmetic products for phthalate esters. *J.Cosmet. Sci*. 57 (2) (2006) 127-37.

[3] A. Manayi, M. Kurepaz-mahmoodabadi, A.R. Gohari, Y. Ajani and S. Saeidnia, Presence of phthalate derivatives in the essential oils of a medicinal plant Achillea tenuifolia, *DARU J. Pharm. Sci*. 22 (2014) 1-6.

[4] X. Lv, Y. Hao and Q. Jia, Preconcentration procedures for phthalate esters combined with chromatographic analysis. *J. Chromatogr. Sci.* 51 (2013) 632-44.

[5] K.E. Kelley, S. Hernández-Díaz, E.L. Chaplin, R. Hauser, A.A. Mitchell, Identification of phthalates in medications and dietary supplement formulations in the United States and Canada. *Environ. Health Perspect*. 120 (3) (2012) 110-116 .

[6] H.Chen, C. Wang,X. Wang, N.Hao and J. Liu, Determination of phthalate esters in cosmetics by gas chromatography with flame ionization detection and mass spectrometric detection. *Int. J. Cosmet. Sci.* 27 (4) (2005) 205-10 .

[7] D. Koniecki, R. Wang, P.R. Moody and J. Zhu, Phthalates in cosmetic and personal care products: concentrations and possible dermal exposure. *Environ. Res*. 111(3) (2011) 329-36.

[8] G. Navaranjan, T.K. Takaro, A.J. Wheeler, M.L. Diamond, H. Shu, M.B. Azad, A.B. Becker, R. Dai, S.A. Harris, D.L. Lefebvre, Z. Lu, P.J. Mandhane, K. McLean, T.J. Moraes, J.A. Scott, S.E. Turvey, M.R. Sears, P. Subbarao and J.R. Brook, *J. Expo. Sci. Environ. Epidemiol*. 30 (2020) 70–85.

[9] S.H. Kim, M.J. Park, Phthalate exposure and childhood obesity. *J. Pediatr. Endocrinol. Metab*. 19 (2) (2014) 69-75.

[10] B. Prasad, Phthalate pollution: environmental fate and cumulative human exposure index using the multivariate analysis approach, *Environ. Sci.: Process. Impacts* 23 (2021) 389-399.

[11] J. Apau, W. Sefah and E. Adua, Human contact with phthalates during early lifestages leads to weight gain and obesity, *Cogent Chem.* 6 (2020) 688-701.

[12] L. Lucaccioni , V. Trevisani, E. Passini, B. Righi, C. Plessi, B. Predieri and L. Iughetti, Perinatal exposure to phthalates: from endocrine to neurodevelopment effects, *Int. J. Mol. Sci*. 22 (2021) 4063.

[13] I. Lee, J.Y. Park, S.Kim, J. Nam –An, J. Lee, H. Park, S. K. Jung, S.Y. Kim, J. P. Lee and K. Choi, Association of exposure to phthalates and environmental phenolics with markers of kidney function: Korean National Environmental Health Survey (KoNEHS) 2015-2017, *Environ. Int.*143(2020)105877.

[14] A. Moeller, K.H. Carlsen, P.D. Sly, E. Baraldi,G. Piacentini, I.Pavord, C. Lex and S. Saglani, Monitoring asthma in childhood: lung function, bronchial responsiveness and inflammation, *Eur. Respir. Rev*. 24 (2015) 204–215.

[15] M. Mariana, J. Feiteiro, I. Verde, E. Cairrao, The effects of phthalates in the cardiovascular and reproductive systems: A review. *Environ. Int*. 9492016)758-776.

[16] P.R. Hannon and J.A. Flaws, The effects of phthalates on the ovary. *Front. Endocrinol*. 6 (2015) 8-11.

[17] K.A. Baken, N. Lambrechts, S. Remy, V. Mustieles, A. Rodríguez-Carrillo, C.M. Neophytou, N. Olea and G. Schoeters, A strategy to validate a selection of human effect biomarkers using adverse outcome pathways: Proof of concept for phthalates and reproductive effects, 175 (2019) 235-256.

[18] H.Y. Shen, H.L. Jiang, H.L.Mao, G. Pan, L. Zhou and Y.F. Cao, Simultaneous determination of seven phthalates and four parabens in cosmetic products using HPLC-DAD and GC-MS methods. *J. Sep. Sci.* 30 (1) (2007) 48-54.

[19] L. Liu, Z. Wang, S. Zhao, J. Duan, H. Tao and W. Wang, et al. Determination of total phthalate in cosmetics using a simple three-phase sample preparation method. *Anal. Bioanal. Chem.* 410 (4) (2018) 1323-1331.

[20] J.Qiao, M. Wang, H. Yan and G. Yang, Dispersive solid-phase extraction based on magnetic dummy molecularly imprinted microspheres for selective screening of phthalates in plastic bottled beverages. *J. Agric. Food Chem*.62 (13) (2014) 2782-2789.

[21] Y.Cai, Y.E. Cai, Y. Shi, J. Liu, S. Mou and Y. Lu, A liquid–liquid extraction technique for phthalate esters with water-soluble organic solvents by adding inorganic salts. Microchim.Acta 157 (1-2) (2007) 73-79.

[22] Y.Fan, H. Chen, H. Liu, F. Wang, S. Ma and A. Latipa, , et al. Analysis of phthalate esters in dairy products—a brief review. *Anal. Methods* 9 (3) (2017) 370-380.

[23] A. Andrade-Eiroa, M. Canle and V. Leroy-Cancellieri, V. Cerdà, Solid-phase extraction of organic compounds: a critical review. Part II. *TrAC Trends Anal. Chem*. 80 (2016) 655-67.

[24] J. González-Sálamo, B. Socas-Rodríguez and J. Hernández-Borges, Analytical methods for the determination of phthalates in food. *Curr. Opin. Food Sci.* 22 (2018) 122-136.

[25] J.G. Wu, Determination of eleven phthalate esters using HPLC and UV diode-array detector with liquid-liquid extraction or on line preconcentration. *J.Environ. Sci.Health Part A*. 26 (8) (1991) 1363-1385.

[26] N. Razavi and A. Sarafraz Yazdi, New application of chitosan-grafted polyaniline in dispersive solid-phase extraction for the separation and determination of phthalate esters in milk using high-performance liquid chromatography. *J. Sep. Sci.* 40 (8) (2017) 1739-1746.

[27] A. Kiani, M. Ahmadloo, N. Shariatifar, M. Moazzen, A.N. Baghani and G.J. Khaniki, et al. Method development for determination of migrated phthalate acid esters from polyethylene terephthalate (PET) packaging into traditional Iranian drinking beverage (Doogh) samples: a novel approach of MSPE-GC/MS technique. *Environ. Sci. Pollut. Res. Int.* 25 (13) (2018) 2728-12738.

[28] S.H. Jeon, Y.P. Kim, Y. Kho, J.H. Shin, W.H. Ji and Y.G. Ahn, Development and Validation of Gas Chromatography-Triple Quadrupole Mass Spectrometric Method for Quantitative Determination of Regulated Plasticizers in Medical Infusion Sets. *J. Anal. Methods Chem.*(2018).

[29] A. Zendegi-Shiraz, Z. Es'haghi and M. Hassanzadeh-Khayyat, Synthesis and characterization of composite polymer, polyethylene glycol grafted flower-like cupric nano oxide for solid phase microextraction of ultra-trace levels of benzene, toluene, ethyl benzene and o-xylene in human hair and water samples. *J. Chromatogr. A.* 1418 (2015) 21-28.

[30] J. Feng, M. Sun, Y. Bu and C. Luo, Nanostructured copper-coated solid-phase microextraction fiber for gas chromatographic analysis of dibutyl phthalate and diethylhexyl phthalate environmental estrogens. *J. Sep. Sci*. 38 (1) (2015) 128-33.

[31] N.Adhoum and L. Monser, Removal of phthalate on modified activated carbon: application to the treatment of industrial wastewater. *Sep. Purif. Technol*. 38 (3) (2004) 233-239.

[32] S.Zheng, X. Li, X., Y.Zhang, Q. Xie, Y.S. Wong and W. Zheng, et al. PEG-nanolized ultrasmall selenium nanoparticles overcome drug resistance in hepatocellular carcinoma HepG2 cells through induction of mitochondria dysfunction. *Int. J. Nanomedicine* 7 (2012) 3939-49.

[33] H. Siddiqui, M. Qureshi and F.Z. Haque, Surfactant assisted wet chemical synthesis of copper oxide (CuO) nanostructures and their spectroscopic analysis. Optik 127 (5) (2016) 2740-2747.

[34] S.Taghavi Fardood and A. Ramazani, Green synthesis and characterization of copper oxide nanoparticles using coffee powder extract. *J. Nanostructures*. 6 (2) (2016) 167-71.

[35] J.C.Hubinger and D.C. Havery, Analysis of consumer cosmetic products for phthalate esters J. *Cosmet. Sci.* 57 (2003) 127-137.

[36] S. Cavar Zeljkovic, S. Becirovic, A. Goga and M.Kezic, Influence of Solvent and Extraction Type on Phthalate Determination in Cosmetic Products. *Anal. Chem.Lett.* 4 (2014) 313-318.

[37] H. Chen, C. Wang , X. Wang , N. Hao and J. Liu, Determination of phthalate esters in cosmetics by gas chromatography with flame ionization detection and mass spectrometric detection. *Int. J. Cosmet. Sci.* 27 (2005) 205-210.

[38] D.Koniecki, R.Wang, R.P. Moody and J. Zhu, Phthalates in cosmetic and personal care products: concentrations and possible dermal exposure, *Environ. Res.* 111 (2011) 329-336.

[39] J.C. Hubinger, A survey of phthalate esters in consumer cosmetic products. *J. Cosmet. Sci*. 61(2010)457-465.

[40] H. Guo, N. Song, D. Wang, J. Ma and Q. Jia, A modulation approach for covalent organic frameworks: Application to solid phase microextraction of phthalate esters. *Talanta* 198 (2019) 277-283.

[41] Z. Mehrani, H. Ebrahimzadeh, E. Moradi, Poly m-aminophenol/nylon 6/graphene oxide electrospun nanofiber as an efficient sorbent for thin film microextraction of phthalate esters in water and milk solutions preserved in baby bottle. *J. Chromatogr. A* 1600 (2019) 87-94.

[42] Y. Tong, X. Liu and L. Zhang, Green construction of Fe3O4@ GC submicrocubes for highly sensitive magnetic dispersive solid-phase extraction of five phthalate esters in beverages and plastic bottles. *Food Chem*. 277 (2019) 579-585.

کاربرد نانوذرات پلی اتیلن گلیکول پیوند داده شده با CuO در استخراج فاز جامد فتالات استرها در شامپوی کودک و شوینده ی بدن

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چکیده

این مطالعه شناسایی و تعیین فتالات استرها در نمونه های آرایشی را مورد توجه قرار داده است. از استخراج فاز جامد پراکنده قبل از آنالیز کروماتوگرافی مایع با عملکرد بالا ، برای استخراج آنالیت استفاده شد. جاذب جامد برای استخراج، پلی اتیلن گلیکول بود که روی نانوذرات اکسید مس پیوند زده شد. این جاذب ابتدا سنتز و سپس با میکروسکوپ الکترونی روبشی (SEM) ، پراکندگی انرژی اشعه ایکس (EDX) و طیف سنجی مادون قرمز با تبدیل فوریه (FT-IR) مشخصه یابی شد و سپس برای استخراج آنالیت ها به کار گرفته شد. شرایط استخراج مانند مقدار جاذب ، نوع و حجم حلال واجذب ، زمان استخراج و واجذب و pHمحلول نمونه بهینه شد. اعتبار سنجی روش انجام شد و در شرایط بهینه دامنه های خطی ۰,۰۰۵-۴ میکروگرم بر میلی لیتر با ضریب همبستگی (R2) در محدوده ۰,۹۹۱۴-۰,۹۹۶۲ بدست آمد. حد تشخیص ها بین (LODs) ۰/۰۰۵-۰/۰۰۲۵ میکروگرم بر میلی لیتر و تکرارپذیری قابل قبول (RSD) های زیر ۶,۴۵٪ ، (n =۵) بدست آمد. کاربرد روش پیشنهادی با استخراج فتالات ها در شامپوی بچه و شوینده ی بدن مورد بررسی قرار گرفت که نتایج رضایت بخشی حاصل شد.

واژه‌های کلیدی

فتالات استر؛ HPLC؛ شامپو بچه؛ شوینده بدن؛ نانو ذرات اکسید مس پیوند داده شده با پلی اتیلن گلیکول.