Determination of Bisphenol A in Bottled Mineral Water and Toy Samples by Nanoparticle Assisted Fabric Phase Sorptive Extraction (NFPSE) -High Performance Liquid Chromatography

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Abstract
In recent years, the presence of bisphenol A in food, drinking water, and toys is considered as a toxic compound. In this research, a Fabric-phase sorptive extraction using an organic-inorganic coating as an adsorbent was used to separate bisphenol A in different samples. The isolated bisphenol A was measured by high-performance liquid chromatography. The organic-inorganic coating was done with other methods. Optimal conditions for selecting the type of fabric and bis phenol A extraction were obtained by the central composite design in 3 and 5 variables according to the response surface methodology. At first, the influencing factors in NFPSE such as fabric type, number of sol-gel connections, and binding time were investigated. Also, the effects of different parameters on adsorption such as sample volume, adsorption time, solution desorption volume, desorption time and pH were examined. The calibration curve in the region (0.1-15 ng.mL^{-1}) for bisphenol A was linear with a correlation coefficient of more than 99%.The detection limit (LODs)andthe limit of quantificationwere 0.11 ng.mL^{-1} and 0.37 ng.mL^{-1} respectively.Repeatability (RSD) with three replicated experiments was 1.25%.The recovery was obtained for different samples in the range of 95 to 97 %. According to the obtained results, the method mentioned in this research can be introduced as a reproducible method with a high absorption capacity for bisphenol A determination in drinking water and toys.

1.INTRODUCTION
In today's society, plastic materials have widespread usage in daily lives and industries. Utilizing plastics in the manufacture of food storage containers, bottled waters, and toys has increased dramatically over the past decade due to their unique properties such as strength, tensile strength, and low density. Bisphenol A (BPA) is one of the chemicals used in producing plastics and epoxy resins [1]. It's one of the endocrine-disrupting compounds which have a destructive effect on cellular function through genomic and non-genomic estrogen signaling pathways [2]. BPA contained in food storage containers, bottled waters, and toys, based on researches, is the cause of BPA entering the human body which results in hormonal problems like childhood obesity and male infertility [3]. Factors such as heat and exposure to acidic/alkaline compounds could hydrolyze the ester bonds of BPA and subsequently lead to its entry into the food chain and bottled water sources [4]. In this regard,

various laws and regulations have been made to reduce BPA levels in food, bottled waters, and toys in Europe and the United States, for example, determining 0.04 mg.mL^{-1} in toys for children less than three years of age by the EU [5]. Accordingly, research on sensitive methods of diagnosing and determining BPA levels in different environments are required. In the past few years, several studies have been reported on determining BPA levels in different environments. Among them, the following can be mentioned: HPLC–MS, GC–MS, HPLC, or HPLC-FLD spectroscopy [6]. Various methods for determining traces of BPA and extracting BPA from toys and water resources have been investigated due to low BPA levels in these studies [7].

In the meantime, graphene and its functionalized derivatives have been used as a suitable BPA adsorbent [8]. Graphene is a carbon-based nanomaterial with an extended honeycomb network that has been extensively used in many fields due to its unique chemical and physical

properties. The mechanical, thermal, and electrical properties of graphene and graphene oxide (GO) are significant. GO has a theoretical surface area of 2600 m^2g^{-1}. There are various oxygen-containing functional groups such as hydroxyl and epoxy on the surface of the graphene sheets and carboxylic acid groups on the edges of the sheets, which allow GO changing its performance [9]. Due to the presence of carboxylic groups on the edges of the sheet and in order to increase the amount of these groups Williams' synthesis is used [10].Williams's method can convert some hydroxyl groups to carboxylic groups, which leads to an increase in binding sites and the conversion of GO to a strong adsorbent. In this regard, functionalization by covalent and non-covalent methods can be employed to stabilize the functional groups. In this field, polyethylene glycol (PEG) has gained more attention as a stabilizer [11].

A new sample preparation method, with high sensitivity and widespread uses, called fabric phase sorptive extraction (FPSE), was proposed by Kabir and Furton (2014) [12]. In this method sol-gel was employed as an adsorbent and fabric as a substrate. FPSE method has several advantages, including high contact surface, the strong chemical bond between adsorbent, and substrate, fabric permeability, and high adsorption capacity due to its composite compound, complete extraction, no decrease in performance of aqueous solvents and concentrated chemicals and the possibility to use both hydrophilic and hydrophobic substrates [13]. In this research, we decided to invent a new extraction method by modifying the FPSE method using nanoparticles. Despite the many advantages mentioned for FPSE method such as high primary contact surface area, high sample loading capacity, rapid interaction between analyte-adsorbent, the possibility of choosing various adsorbent solvents according to the measuring device, also the solvent compatibility with gas chromatography as well as liquid chromatography, etc. Fabric phase sorptive extraction (FPSE) has slowly but surely become more widespread as a novel extraction technique for its advantages. But, two main limitations have been addressed by FPSE, long sample preparation time and lack of good reproducibility due to slight changes in the fabric texture from one piece to another. Fabric reinforcement with nanocomposite is a new and effective opening idea that can significantly improve the separation results with this method .In this research, by consolidation the structure of the fabric coating with nanoparticles, we were able to provide a stronger and more practical adsorbent. Incorporation of nanoparticles into the FPSE makes the benefits of this method improve dramatically, and gives it more features such as the high loading capacity, the significant increase in the porosity of the adsorbent and its

contact surface with the analyte, and more selectivity. In addition, NFPSE creates a new and powerful method which allows us to utilize all the extraction phases available for both solid phase extraction and solid phase microextraction. This study aimed to investigate a rapid and sensitive sample preparation method using the unique properties of functionalized GO by PEG along with sol-gel, as an adsorbent, in a nanoparticle assisted fabric phase sorptive extraction technique (NFPSE)combined with high-performance liquid chromatography to measurement BPA in aqueous solutions and toys.

2.EXPERIMENTAL

2.1.Chemicals and reagents
All chemicals were of analytical grade. Reagents used for the synthesis were included ingredients of sol-gel (Tetraethyl orthosilicate) TEOS, (Tris hydroxymethyl aminomethane) TRIS and methanol. Also, general solvents (ethanol, methanol), and reagents to prepare graphene oxide (graphite, sulfuric acid, potassium permanganate, hydrogen peroxide, hydrochloric acid), polyethylene glycol (PEG 4000), bisphenol A, N-dimethylformamide anhydrous (DMF), tetrahydrofuran anhydrous (THF), pyridine, acetonitrile and thionyl chloride were supplied by Merck (Darmstadt, Germany). Substrates for fabric phase sorptive extraction media were prepared from local markets, Neyshabour, Iran. Stock standard analyte solutions made in methanol at a concentration of 1000 $mg.mL^{-1}$. Standard solutions used were made daily by dilution of the stocks in deionized water or methanol as required. Different bottled water samples prepared from the local supermarkets were investigated. The toys were purchased from a local toy store. All samples were stored in the dark at 4 °C until use.

2.2.Instrumentation
An HPLC system (Waters 1525, USA) with a UV-VIS (Waters 2489) variable wavelength detector was used for analysis. A waters C18 column (4.6 × 250 mm, 5 μm) was applied to separate the target analytes. A Thermo-Scientific Nicolet IR100 (Shimadzu, Tokyo, JAPAN) Fourier-transform infrared (FTIR) spectrometer was applied to investigate the surface structure of graphene oxide, GO-CL, and GO-PEG nanoparticles. The spectra were recorded in the range of 400–4000 cm^{-1}. Dry samples were mixed with KBr and were made in the form of tablets. Ultrasonic bath sonicator (backer, VCLEAN1-L2) was used for ultrasound treatments. SEM images were taken using a field emission scanning electron microscope (FE-SEM) with an acceleration voltage of 15.0 kV and different resolutions of 2 μm and 10 μm. The pH

of the samples was measured using a Metrohm pH meter (Model827 pH-lab, Switzerland).

2.3.Collection and presentation of data
Experimental design according to a standard orthogonal array and statistical Correction of the results was carried out by Design expert software for 3D curves. Optimal conditions for extraction were got by the central composite design according to the response surface methodology.

2.4.Preparation of nanoparticle assisted fabric phase sorptive extraction media
Pretreatment of fabrics: First segments of cellulose fabrics (100 cm^2) were soaked with deionized water for 15 min under sonication. To remove chemical contamination, the fabrics were washed with a lot of deionized water and treated with 0.1 M NaOH solution for 1 h under sonication. Then the prepared fabrics were washed several times with deionized water and treated with 0.1 M HCl solution for 1 h and sonicated in the same order as before. Next, the treated fabrics were washed with a lot of deionized water and dried in ambient atmosphere for one night. The dried fabrics were hold in clean glass containers until they covered with sorbents [19].

Synthesis of graphene oxide: Graphene oxide nanoparticles were synthesized by a chemical procedure called the modified Hummer method [10]. Initially, 2 grams of graphite powder was added to 45 ml of H$_2$SO$_4$ (98 %) and was stirred for 2 hours. Then 6 grams of KMnO$_4$ slowly was added to the solution. During this period the temperature was kept at less than 20°C. The solution was stirred at 35°C for 2 hours. The final solution was diluted by adding 90 ml of deionized water with vigorous stirring. Then, 10 ml of H$_2$O$_2$ (30 %) and 150 ml of deionized water were added to the solution, and the resulting suspension was centrifuged. The sediment (graphite oxide) was washed with 50 ml of 5% hydrochloric acid and then with deionized water several times to reach pH 7.

At the end, by adding 160 ml of water to the graphite oxide and ultrasonication for 1 hours, graphite oxide layers were separated and graphene oxide was obtained as a single monomolecular layer of graphite oxide [14]. The structure of the synthesized graphene oxide was examined by scanning electron microscopy. In the obtained images, the graphene oxide layers were evident. Also, the chemical structure of the samples was characterized by the use of XRD and FT-IR analysis.

Preparation of acyl chloride-functionalized graphene oxide: First, the acyl-chloride functionalized GO was gained via the activation of carboxylic groups and part of hydroxyl groups on

the GO by using thionyl chloride. For this purpose, the mixture included 20 ml of DMF and 2 grams of GO -powder was sonicated for 2 hours. To convert carboxyl group (-COOH) on the GO surface to an acyl chloride (GO-Cl), 60 ml of thionyl chloride (0.82 mol) was used and reaction earnings at 60 °C for five days to convert carboxyl group (COOH) on the GO surface to GO-Cl. The GO-Cl product obtained was washed with THF, centrifuged, and then dried [15,16].

Preparation of PEG – functionalized GO: The 10 ml of DMF was composed with 200 mg GO-Cl made in the previous step. To create single sheets the (GO-Cl)/DMF, this solution was sonicated for 30 minutes to exfoliate the specific sheets. Then, 5.0 mL of pyridine and 2.0 g of PEG 4000 were added to this solution. The resulting solution was stirred at 120°C for three days. The product was washed with ethanol and filtered. At the end, the resulting powder was dried at 60°C [16,17].

Preparation of sol for coating the substrate: The sol-gel nanocomposites were made according to a method that had formerly been done. Briefly, the sol solution was created by stirring 700µL of TEOS and 137.5 µL of (Tris hydroxymethyl amino methane) tris solution in water (5:95 v/v) as an alkaline catalyst for 5 minutes by ultrasonic waves. Then 500 µL of PEG-GO in methanol were added to the mixture. To complement the hydrolysis procedure, the mixture was located under ultrasonic waves for 5 minutes. Finally, the sol solution was carried over to a clean (60 mL) glass bottle.

Formation of sol-gel GO-PEG coatings on the substrate: Cellulose fabric was used as the optimal substrate for the sol-gel GO-PEG cover. The neat and treated fabrics were placed in the sol solution so that a three-dimensional network of sol-gel made based on GO-PEG can be built overall the porous substrate matrix. The fabrics were placed inside the sol solution for 10 min, then fabrics were dried, this process was repeated twice. After completing the coating time, the fabrics were brought out from the solution and the coated fabric was dried and aged at 50 ◦C under the stagnant atmosphere within the desiccator for 1 h. In order to prevent any contamination, the fabric covered with sol-gel was cut into 2 cm × 2.5 cm segments and were stored in a closed glass container.

2.4.Real sample preparation
Different bottled waters and toy samples from supermarkets and toy stores were analyzed. Three samples of water were prepared as follows: 1- bottled water placed in the sun, 2- bottled water placed in the freezer, 3- ordinary bottled waters. The preparation of the toy sample is based on a method similar to the migration conditions of chemicals in the baby's saliva. This method is

regulated by the European Union. Therefore, 10 cubic centimeters of the toy sample is sonicated for 1 hour in 100 cc of distilled water at room temperature. This solution is used to checks the amount of bisphenol in the toy [18]. All the samples were assembled in amber-glass bottles and were kept in the dark at 4 ◦C until experiment.

2.5. Analytical procedure
Description of the experiment: 5 mL of the aqueous standard or real sample (containing 5 mg.mL^{-1} of each analyte) were added to a beaker. In a second step, adjust the pH to 3.0 with hydrochloric acid or sodium hydroxide. Then the treated fabric was placed in the beaker and stirred at an ultrasonic bath sonicator for 10 min. After completion of the extraction process, the fabric was removed from the solution and immersed in 1 mL of methanol/acetonitrile (1:1, v/v) and sonicated at ultrasonic bath for 5 min. The back-extraction solution containing the analytes was injected into the HPLC/UV detector.

2.6. HPLC analysis
Bisphenol A was analyzed on mentioned HPLC system equipped with a UV variable wavelength detector. The C18 column, controlled at 30°C, was used to analyze the aqueous samples. The mobile phase comprised of methanol (60%) and HPLC-grade water (40%). The flow rate was set at 1.0 mL.min^{-1}. The UV detection wavelength was set at 220 nm. Elution chromatography carried out in isocratic modes.10 μL samples were injected into the HPLC system for further analysis.

3. RESULTS AND DISCUSSION
3.1. Chemistry of the NFPSE substrates and the sol-gel coatings
Many of synthetic and natural fabrics for example; cellulose, polyester, nylon, and polyamide were examined for the selection of fabric phase extraction substrate. Cellulose and polyester could be used due to the presence of active functional groups inherently or the creation of functional groups by modifying the surface of the fabric. Therefore, polyester and cellulose fabrics that have inherently active functional groups and the possibility of interaction of these functional groups with sol-gel were selected. In this work, four types of cellulose fabrics were examined.
Cellulose fabric is hydrophilic and polyester fabric is hydrophobic. Fabric texture and type of sol-gel coating are effective factors in selective extraction of analytes with a wide range of polarity. In many cases, tetra methoxy silane (TMOS), and tetra ethoxy silane (TEOS), are used as inorganic precursors in the sol-gel process. Also, PEG-functionalized graphene oxide as a sol-gel reinforcement, was used to increase the entrapment of analytes with different polarity [13].

3.2. Surface chemistry of cellulose substrate
Cellulose is known as a hydrophilic linear polymer of β-D-glucose units. The three hydroxyl functional groups are located indifferent positions of the cellulose dimers. These groups participate in the polycondensation stage during the sol-gel process with different degrees of reactivity [19]. Due to these cases, cellulose is an excellent substrate for modified sol-gel coating. The cellulose fabric applied in this work was activated by the alkaline treatment or mercerization with NaOH (1 M) and neutralization of excess sodium hydroxide with HCl (0.1 M) for an hour under sonication, respectively[20].

3.3. Coating process of sol-gel on the fabric media
The creation of sol-gel, PEG-functionalized graphene oxide coating on cellulose substrate needs various of reactions: (a) hydrolysis of the precursor (TEOS) by catalyst;(b) poly-condensation process; (c) Interpolation of PEG-functionalized graphene oxide accidentally into the evolving sol-gel network; and (d) chemical bonding of the evolving sol-gel network to the flexible cellulose fabric substrate. During the poly-condensation, the evolving sol-gel network reacts with existing surface hydroxyl groups of cellulose and creates a covalently bonded sol-gel hybrid coating that is evenly distributed all over the substrate matrix.According to the literature, sol-gel reinforced with graphene has a high extraction efficiency among chemical adsorbents. This can be considered due to the concurrent presence of μ-μ interaction, hydrogen bonding and London dispersion forces (mainly from the ethyl functional groups of TEOS (–Si–OC2H5)[8]. Also, the essential properties of PEG include solubility in water and organic solvents, steric flexibility, being non-toxic, its high crystalline property has made it a widely used material in the extraction process. In this work, PEG is stabilized in the polymer molecular chain through strong hydrogen bonds with oxygen functional groups on the surface of graphene oxide. This method increases the practical level of GO and thus increases its application in a wide range of reactions. With characteristic high solvent and chemical consistency also highly available active locations for efficient and fast analyte extraction [21,22].Therefore, in addition to the polarity similarity between the adsorbent and the analyte, also other factors such as functional groups attached to the substrate are effective in increasing the extraction efficiency.

3.4. Orthogonal array design and statistical analysis

To achieve maximum efficiency in a process, process execution methods must be upgraded. In modern methods, simplifying a process is one of the critical principles. In the initial simplification methods, the effect of one factor is examined at all times while the other parameters are kept constant. This method is called optimizing one factor at a time. Among the disadvantages of this method are a large number of experiments and the failure to investigate the impact of factors on each other. The response surface method is a numerical information collection system based on the use of polynomial sentences that should show the effect of information indicators to obtain measurable predictions. The purpose of this method is modeling and analyzing the process in which the response of interest is affected by various variables and the objective of this method is to optimize the response [23].

3.5. Selection of the experimental design

The first-order model for the optimization can be displayed follows:

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \varepsilon$$

Where k is the number of variables, β_0 is the fixed content, β_i defines the coefficients of the linear parameters, x_i illustrates the variables, and ε is the residual dependenton the experiments.

This equation is a linear equation for which the reaction does not have a specific curvature or arc. To investigate the impact of quadratic sentences, two-level factorial lines were used. When the effects of quadratic sentences are significant, these effects are fixed. Two-level factorial can be used to examine shape. Polynomial expressions include additional expressions to express the effects of factors on each other.

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{1 \leq i \leq j}^{k} \beta_{ij} x_i y_j + \varepsilon$$

where β_{ij} demonstrates the coefficients of the interaction parameters.

To check the important points (minimum, maximum, etc.), the existence of quadratic sentences according to the existing conditions is necessary in a polynomial.

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \leq i \leq j}^{k} \beta_{ij} x_i x_j + \varepsilon$$

where β_{ii} demonstrates the coefficients of the quadratic parameter [24].

In order to match the quadratic model, the parameters must be active in three levels. In designs related to central and two-level points, The quadratic terms are not well studied.

The response surface program includes experimental design techniques that cause better identify of response and optimize the studied response [25]. There are different types of response surface planes and we have investigated the Central Composite Designs (CCD) in this work. These plans coordinate a complete quadratic model and totalize information from a correctly designed factorial experiment.

3.6. Study of the adsorption variables

In this part, we have applied CCD for two steps; a) optimization of substrate preparation conditions and b) optimization of analyte adsorption. The statistical characteristics of the response, the graphic methods and the response surface plans was investigated.

3.7. Optimization of substrate preparation conditions

The efficiency of a series of primary experiences characterized that we need to assume three critical parameters in four and five-levels in the process of adsorption. Therefore, L56OA experimental design was applied. The factors and their levels considered in this work are shown in Table 1.

3.8. Optimization of fabric phase sorptive extraction (FPSE) conditions

According to the selected experimental design, the L13OA experimental design was used to determine the best extraction conditions. In this design, five factors in three levels were considered Table 2.

3.9. Fitting the model

The experimental data for two steps were shown in Tables 3 and 4. The responses were obtained in the following conditions. Fitting, the data to various models (linear, two-factorial, quadratic and cubic), and their analysis of variance displays that adsorption is most correctly characterized with the quadratic model for the first part and two-factorial for the second part. In the first part, the highest value of R^2 (0.8570) was related to the quadratic model, which was higher than other models. Also, the adjusted R^2 of the quadratic model (0.8081) was higher than linear and two factorial models for all responses. Also, in the second part, the highest value of R^2 (0.9979) was related to the linear model, which was higher than other models. Also, the adjusted R^2 of the quadratic model was (0.9874). These results were showed an acceptable fit of the estimated model with the experimental data. According to research [26, 27], in a good fit, R^2 must be near 1. In this work, R^2 higher than 0.8 was indicated the success of the model in investigating the mechanism. Fig 1 was showed the predicted amount of absorption versus the actual value. The existence of a linear distribution was indicated the appropriateness of the model. The predicted values and the observed values were very close to each other.

3.10. Statistical analysis of variance (ANOVA)

Analysis of variance is used to examine the model's accuracy, the effect of each factor, and the

interaction of factors. The results of ANOVA Show in the Tables 5 and 6. Each factor on the table that has the least P-value (among that have a P-value of smaller than 0.05) is one the most important [28]. In both tables, the models with the p-value below 0.05 were statistically significant, indicative the suitability of the model for these experiments. So, in the first table, the factor (type fabric) can be known as the most in fluential, and factor (number of connections) may be recognized as a meager one. Also, in the second part, factor (desorption volume) was influential factor and (sample volume) was recognized as a meager one.

3.11. Effect of independent and interactive parameters on extraction

The influential factors in the extraction were determined according to the ANOVA tables and the influence coefficients of each factor in parts 1 and 2. In the first part, the type of fabric was determined as the most influential factor Fig 2a. Cellulose as a hydrophilic substrate with hydroxyl groups can take part in polycondensation within the sol-gel coating process at a different degree of reactivity. As such, cellulose represents to be a superb candidate as a potential substrate for sol-gel sorbent coating [19]. In the second part, the most excellent effect was related to desorption solvent Fig 2b. According to the table of the impacts, the amount of extraction was increased with the reduction of the volume of desorption solvent. This result was due to the high concentration of the analyte desorbed by the fabric solvent in the small amount of desorbed solution.

The effect of interaction between factors, i.e., in the first step, connection time and fabric type on extraction was illustrated by the diagram of interaction was obtained from the model. Also, the 3D response surface produced by the model, as displayed in Fig 3. At this stage, it can be concluded that the type of fabric and also the connection time with sol-gel have a significant impact on the extraction process. In the second part, the effect of interaction between parameters, for example, sample volume and adsorption time on extraction, was illustrated by a contour plot and 3D response surface obtained from the model, as displayed in Fig 4. According to the obtained results, this effect of interaction has the most significant impact on the extraction process [29].

Table 1. The factors and their levels in substrate preparation conditions

Factor	Name	Minimum	Maximum	Coded low	Coded high	Mean
A	Number of connections	2	10	-1	+1	15
B	Time of connection	5	25	-1	+1	20
C	Type of fabric	Categoric: 1, 2, 3, 4				

Table 2. The factors and their levels in fabric phase sorptive extraction (FPSE) conditions

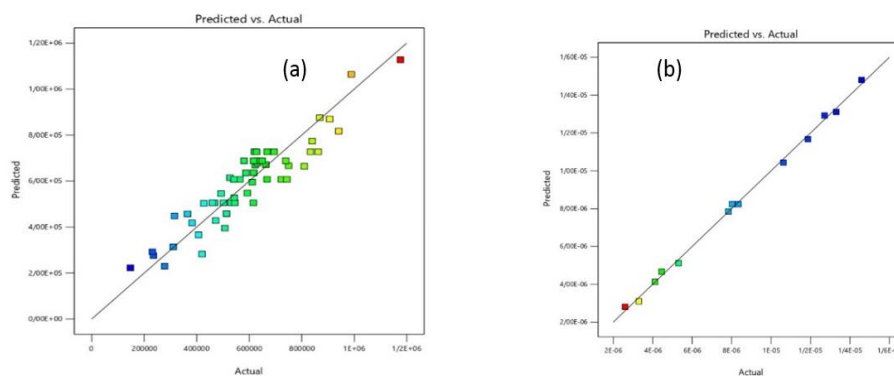| Factor	Name	Minimum	Maximum	Coded low	Coded high	Mean
A	Sample volume	5	15	-1	+1	15
B	Adsorption time	10	20	-1	+1	20
C	Desorption volume	1	3	-1	+1	3
D	Desorption time	5	15	-1	+1	15
E	pH	3	11	-1	+1	11

Fig. 1. Predicted amount of adsorption versus the actual value, (a) substrate preparation parameters, (b) fabric phase sorptive extraction (FPSE) parameters
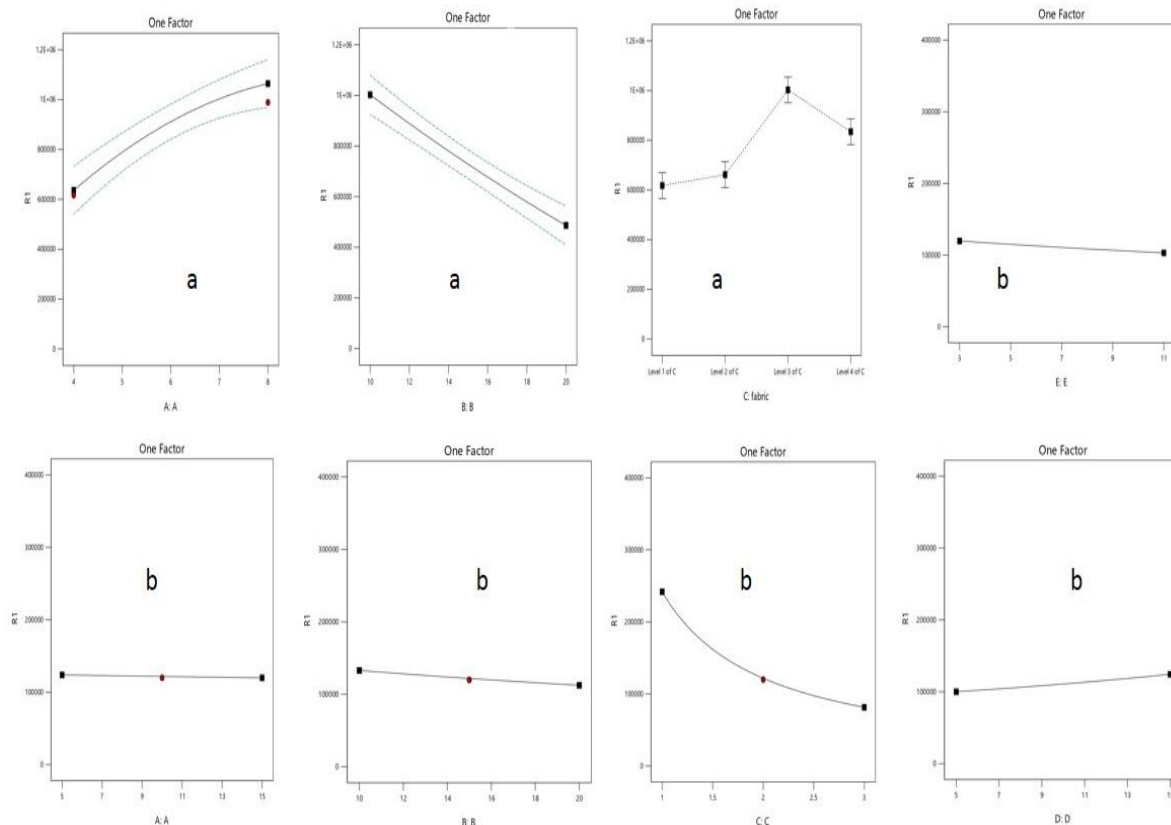
Fig. 2. (a) The effect of independent substrate preparation parameters on extraction (A, B, C). (b) The effect of independent NFPSE parameters on extraction (A-E)
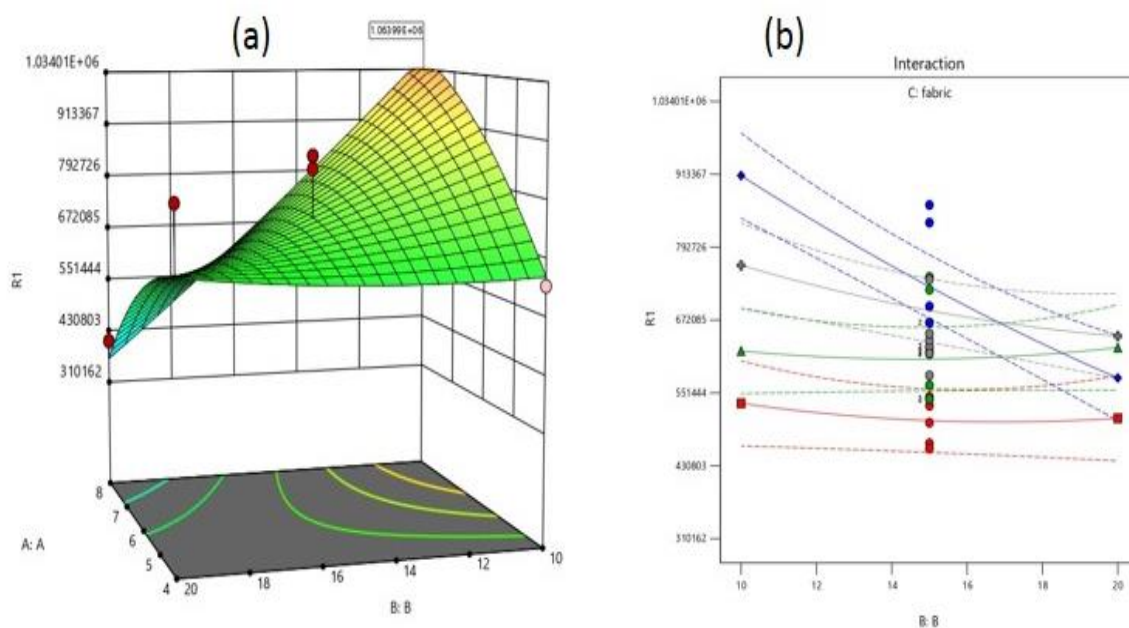

Fig. 3. The Effect of substrate interactive parameters on extraction: (a) 3D response surface (b) diagram of interactions
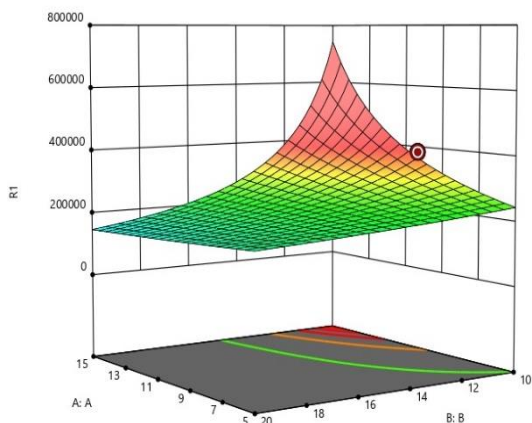
Fig. 4. The effect of experimental interactive parameters on the extraction, 3D response surface
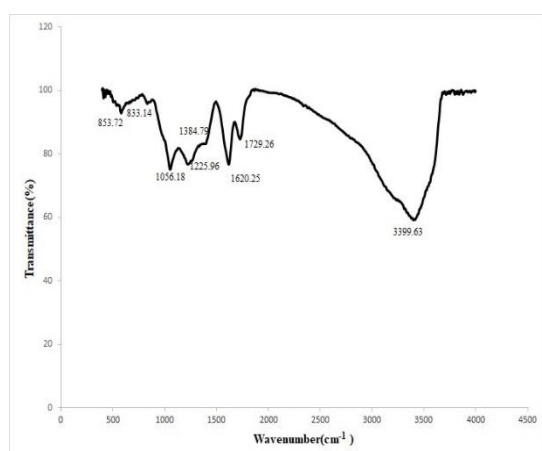

Fig. 5. FT-IR spectra of GO

3.12. Optimization of desorption solvent

The effect of desorption solvent on extraction was studied using methanol, acetonitrile, and a (1:1 v/v) mixture of acetonitrile/methanol. Due to the medium polarity of bisphenol A, 1mL of methanol (MeOH, relative polarity 0.762), acetonitrile (CAN, relative polarity 0.46), or the methanol-acetonitrile mixture (MeOH: CAN, 50:50 v/v) were applied for desorption of BPA from NFPSE media. The highest adsorption was observed in the extraction process with a methanol-acetonitrile mixture (MeOH: CAN, 50:50 v/v).This can be due to the moderate polarity of methanol-acetonitrile mixture [19].

3.13. Characterization study

FT-IR spectra of GO:
The FT-IR spectra of GO material were shown in Fig 5. The spectrum of GO illustrates the entity of some generic peaks, corresponding to O-H stretching (3399.6 cm^{-1}), C=O stretching from -C=O and -COOH (1729 cm^{-1}), C=C stretching (1620 cm^{-1}), C-O stretching (1384cm^{-1}), and C-O-C stretching (1056cm^{-1}) [30].

Table 3. L56OA experimental design

Run	Factor A Number of connections	Factor B Time	Factor C Type fabric	Response
1	6	15	3	833408
2	6	15	4	616907
3	6	15	1	545209
4	6	15	3	694855
5	6	5	2	750164
6	4	10	3	616938
7	4	10	2	315650
8	6	15	2	541502
9	6	15	2	540982
10	2	15	3	382597
11	6	15	4	580431
12	6	25	2	630763
13	8	10	4	868600
14	6	15	1	615829
15	6	25	3	364928
16	6	15	1	459272
17	6	5	4	906232
18	2	15	4	513550
19	6	15	1	502026
20	10	15	3	592782
21	6	15	2	564173
22	8	10	2	663324
23	10	15	4	471957
24	4	20	4	839825
25	2	15	2	427072
26	6	15	2	667706
27	6	15	3	627711
28	6	5	1	611533
29	6	15	4	649731
30	8	20	2	310757
31	6	25	4	587288
32	4	20	2	940613
33	4	20	3	809723
34	4	10	1	235608
35	8	10	3	988726
36	6	15	2	722263
37	6	25	1	492987
38	8	20	4	507340
39	6	15	1	468037
40	6	15	2	743467
41	6	5	3	1.1E+06
42	6	15	3	862615
43	6	15	4	739124
44	4	10	4	542935
45	8	20	3	407109
46	4	20	1	526724
47	2	15	1	277733
48	10	15	2	147604
49	6	15	1	530232
50	10	15	1	231093
51	6	15	4	628207
52	6	15	4	639124
53	8	20	1	420466
54	6	15	3	620002
55	6	15	3	667970
56	8	10	1	622647

FT-IR spectra of GO-PEG:
Seeing the FTIR spectrum of GO-PEG, the major absorption peaks of GO are preserved in GO-PEG

with a small shift of peak positions and relative change of intensity. Additionally, as there are C=O and O–H groups in GO-PEG, FTIR curve represents the ester bonding between PEG carboxyl groups and GO. These are the signatures of functional groups of GO, and GO-PEG which confirm the successful conjugation of GO-PEG.

In the FTIR spectra of GO-PEG, the peak of hydroxyl group in the GO surface was shifted from 3399 cm^{-1} to 3450 cm^{-1} Fig 6. The peak of the C-H groups was also observed in 2829cm^{-1}. These shifts indicate the successful connection of the PEG to the surface of the GO edges. The peaks appearing at 1568.8, 1403.9 and 1193.2 cm^{-1}was indicated the existence of carbonyl groups, C = C bonds, and C-O [16].

Scanning electron microscopy for surface morphology:

Scanning electron micrographs of (a) uncovered surface of cellulose fabric substrate at ×200 magnification,(b)fabric coating with sol-gel reinforced by PEG-functionalized graphene oxide at ×200 magnification, (c) graphene oxide at ×200 magnification, and(d) PEG-functionalized graphene oxide at ×200 magnification was shown in Fig 7. The SEM images illustrated that the surface of cellulose fabric is highly organized with repetition packets of fibers braided to form a porous structure. The GO-PEG reinforced sol-gel sorbent is homogeneously diffused on the cellulose fabric substrate in the form of nanoparticles and bores in the sol-gel covered surface remain wholesome. In this case, the through-pores of the fabric substrate are not blocked by sol-gel/GO-PEG, so the aqueous sample matrix passes quickly through the fabric and the extraction is balanced in a short time. The SEM image of coated cellulose also displayed the high loading of the sorbent on the substrate. The SEM images of GO synthesized by a modified Hummers method clearly indicated the two-dimensional sheet-like structure of GO. Also, should pay attention to the greater thickness of the GO sheets at the edges. This is due to the combination of oxygen-containing functional groups at the edges of the GO. SEM images show the GO modified sheets suspended [31].

XRD spectra of GO:

XRD analysis was applied to characterize the crystalline nature and phase purity of the as-synthesized GO. Due to the XRD pattern of the graphite, a refraction peak at 2Θ = 26.30 related to an interlayer spacing of about 0.34 nm [32]. According to the sample XRD pattern Fig 8, with increasing oxidation levels, the peak at 2Θ = 26.30 intensity initially decreases and eventually disappears at higher oxidation levels 2Θ = 10.650. Also, a new peak at a lower diffraction angle is observed that grow with increasing oxidation levels corresponding to the diffraction pattern of

GO. According to the XRD pattern of the synthesized sample is observed significant variations in the crystallinity of GO. The peak broadening effect due to moderate oxidation of graphene is according to the experimental results of [33-35]. With the addition of different types of oxygen-containing groups to the graphene network, interlayer spacing of the GO sample increases.

XRD spectra of GO-PEG:

The XRD method was applied to appraise the effect of GO functionalization. In the GO–PEG spectrum, a peak of about 2Θ =25 was observed, which is the result of GO functionalization. This peak represents a heterogeneous sample that was located in different parts of the GO and was caused some exfoliation in the GO layers (Fig 9).
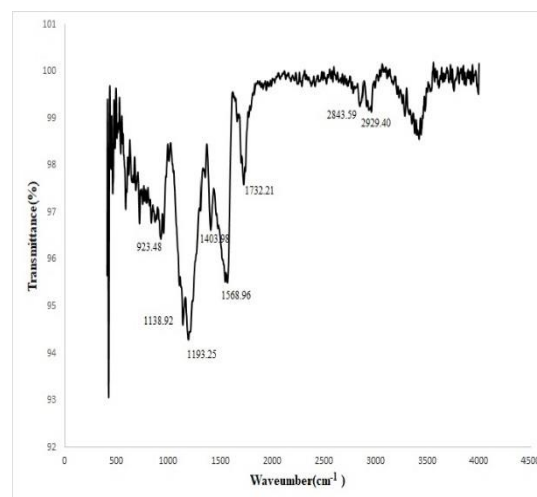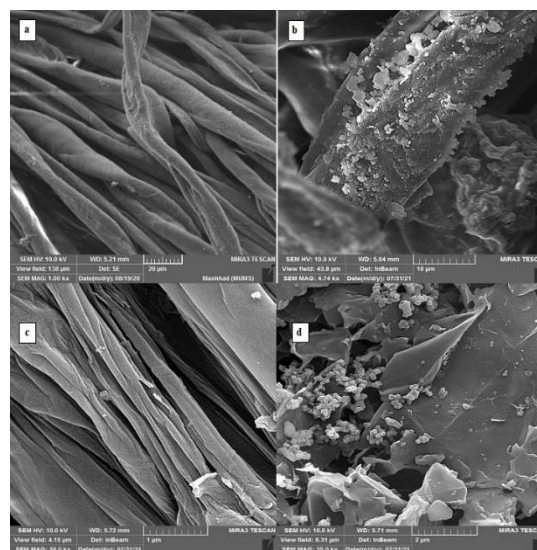

Fig. 6. FT-IR spectra of GO-PEG

Fig. 7. Scanning electron micrographs, (a) uncovered surface of cellulose fabric substrate, (b) FPSE device coating with sol-gel PEG-functionalized graphene oxide, (c) graphene oxide, and (d) PEG-functionalized graphene oxide
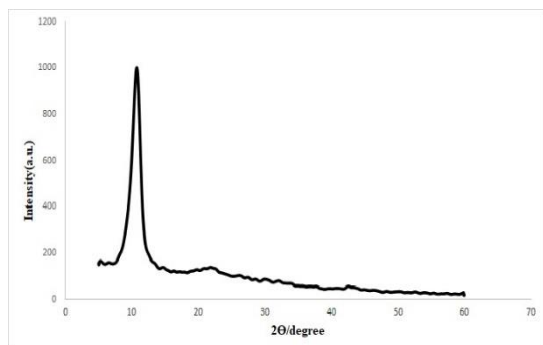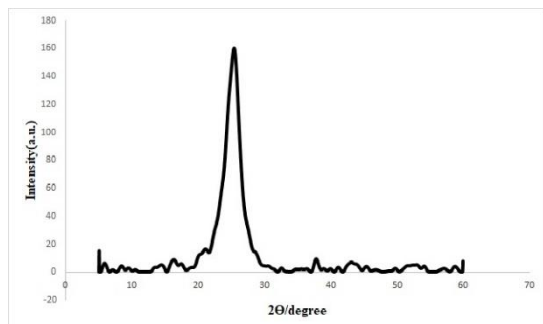
Fig. 8. XRD spectra of GO

Fig. 9. XRD spectra of GO-PEG

3.14. Analytical parameters

Matrix-matched calibration curves from 0.1 to 15 ng mL^{-1} provided acceptable linear ranges for analyte. The method's efficiency was evaluated according to the limit of detection (LOD) and quantification (LOQ). LOD, calculated using a signal-to-noise ratio (S/N) of 3, (0.11) ng.mL^{-1}, while the LOQ, computed using a S/N of 10, 0.37 ng.mL^{-1} (See Table 7). Repeatability (RSD) with three replicated experiments was 1.25%.

3.15. Real sample analysis

To study matrix effects and applicability of the technique to bottled water and toy samples, final tests were accomplished on three water samples that stored in plastic bottles, and one toy sample. The standard solution of bisphenol A was spiked into actual samples to demonstrate the potential of this method as a viable extraction technique for water and toy samples (Fig 10, a: non-spiked real samples of bisphenol A, b: real samples spiked with 1 ngmL^{-1} of bisphenol A). Retention time between 6-8 min is related to bisphenol A. The relative recovery is the ratio of the concentrations found in the surveyed matrix to those in distilled or deionized water spiked with the exact amounts of analyte (1 ng mL^{-1}). It's commonly used instead of complete recovery. Relative recovery percent of 97%, 95% and 94.6% were obtained for bisphenol A in the water samples and 97% in the toy sample. The mentioned method for determining bisphenol A was compared to some reported methods. The comparison results are shown in Table 8. Compared to other methods, this method showed acceptable LOD, LOQ, and recovery.
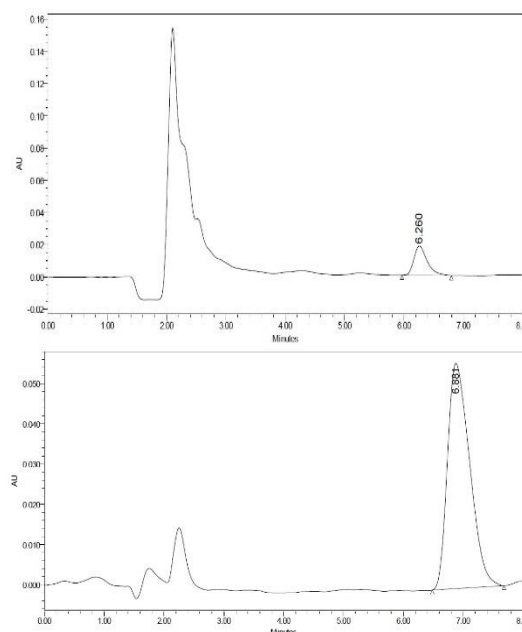

Fig. 10. HPLC chromatograms obtained for (a) non-spiked real sample of bisphenol A and (b) real sample spiked with 1 ng mL^{-1} of bisphenol A.

Table 4. L13OA experimental design

Run	Factor A Sample volume	Factor B adsorption time	Factor C desorption volume	Factor D desorption time	Factor E pH	Response
1	15	10	2	5	11	94097
2	10	15	2	10	7	119844
3	5	10	3	10	11	78678
4	10	10	1	5	3	384234
5	5	15	3	5	3	75166
6	15	20	3	5	7	68562
7	5	10	1	15	7	303401
8	15	15	1	15	11	224455
9	5	20	2	15	3	124590
10	5	20	1	5	11	242665
11	10	20	3	15	11	84268
12	15	20	1	10	3	188353
13	15	10	3	15	3	127584

Table 5. Analysis of variance (ANOVA)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1.847E+12	14	1.319E+11	17.55	< 0.0001	significant
A-A	2.612E+09	1	2.612E+09	0.3474	0.5588	
B-B	1.666E+11	1	1.666E+11	22.15	< 0.0001	
C-fabric	4.033E+11	3	1.344E+11	17.88	< 0.0001	
AB	5.269E+11	1	5.269E+11	70.08	< 0.0001	
AC	7.259E+10	3	2.420E+10	3.22	0.0325	
BC	2.134E+11	3	7.112E+10	9.46	< 0.0001	
A²	3.618E+11	1	3.618E+11	48.13	< 0.0001	
B²	2.534E+10	1	2.534E+10	3.37	0.0736	
Residual	3.082E+11	41	7.518E+09			
Lack of Fit	1.796E+11	21	8.551E+09	1.33	0.2641	not significant
Pure Error	1.287E+11	20	6.434E+09			
Cor Total	2.155E+12	55				
R²	0.8570					
Adjusted R²	0.8081					
Predicted R²	0.7161					
Adeq Precision	20.1594					

Table 6. Analysis of variance (ANOVA)

Source	Sum of Squares	Mean Square	F-value	p-value	
Model	2.006E-10	2.006E-11	95.11	0.0104	significant
A-A	1.844E-13	1.844E-13	0.8741	0.4485	
B-B	4.671E-12	4.671E-12	22.14	0.0423	
C-C	1.642E-10	1.642E-10	778.30	0.0013	
D-D	9.521E-12	9.521E-12	45.13	0.0214	
E-E	4.490E-12	4.490E-12	21.28	0.0439	
AB	2.983E-12	2.983E-12	14.14	0.0640	
AC	2.904E-14	2.904E-14	0.1377	0.7462	
AD	3.081E-12	3.081E-12	14.60	0.0622	
AE	3.820E-12	3.820E-12	18.11	0.0510	
BC	2.370E-12	2.370E-12	11.23	0.0787	
Residual	4.219E-13	2.110E-13			
Cor Total	2.011E-10				
R²	0.9979				
Adjusted R²	0.9874				
Predicted R²	0.8005				

Table 7. Analytical performance of the method

Analyte	r^2	Calibration equation	LOD ($\mu g. mL^{-1}$)	LOQ ($\mu g. mL^{-1}$)	Linearity ($\mu g. mL^{-1}$)	RSD (%)
Bisphenol A	0.9939	y = 103152x	0.113	0.3769	0.0001-0. 015	1.25

Table 8. Comparison of current method with other similar methods applied for determination of bisphenol A.

Extraction technique	Method	LOD ($\mu g mL^{-1}$)	LOQ	Linear range ($\mu g mL^{-1}$)	RSD%	R2	Recovery%	REF
FPSE	HPLC-UV	0.11×10^{-3}	0.37×10^{-3}	0.0001-0. 015	1.25	0.99	94-97	This work
MMSPE	LC-MS/MS	1.8×10^{-6}	6.1×10^{-6}	--	1.4	--	96	[1]
SPE	GC-MS	1.5×10^{-3}	5.1×10^{-3}	0.005-0.2	6.9	0.99	93.9	[36]
SPE	HPLC-FLD	1.9×10^{-3}	--	0.005-5	2.8	0.99	99.4	[37]
SPE	HPLC	$1-2 \times 10^{-3}$	--	0.005-10	1.5	--	90.8	[38]
SPE	HPLC	0.3×10^{-3}	--	--	4.6	0.99	92.5	[39]
SPE	GC-MS	--	--	0.0001-1	--	0.99	93-97	[40]
IL-DLLME	HPLC	0.19×10^{-3}	0.63×10^{-3}	0.0003-0.0005	5.2	0.99	99	[2]
SPE	LC-MS/MS	0.4 µg/kg	1.21µg/kg	0.5-500 µg/kg	1.2	0.99	82-133	[41]
FPSE	HPLC-UV	16.7 µg/kg	50µg/kg	50-5000 µg/kg	8.4-11.2	0.99	90-107	[8]
SPE	HPLC-FL	0.002 µg/kg	--	0.005-10 µg/kg	4.7	0.99	95-100	[4]

4.CONCLUSION

Due to the high use of bisphenol A in bottled waters and toys, researchers have used a lot of research to measure this substance in these samples.

A small amount of this material threatens people's health, especially children. In this work, a new method NFPSE has been investigated to measure small amounts of bisphenol A in water samples stored in plastic bottles and toys.

It is based on the use of nanomaterials to reinforce the sol-gel adsorbent. In this method, with the help of NFPSE along with HPLC-UV detection, have been analyzed the bisphenol A.

Bonding of GO by PEG, as well as the bonding of silica chains on the GO sheets, has caused a significant increase in the specific surface area of adsorbent. NFPSE is suggested as a cost-effective alternative to other microextraction procedures.

REFERENCES

[1] J. Regueiro, and T. Wenzl, Determination of bisphenols in beverages by mixed-mode solid-phase extraction and liquid chromatography coupled to tandem mass spectrometry, *J Chromatogr A*. 1422 (2015) 230-38.

[2] Y. Vicente-Martínez, M. Caravaca, and A. Soto-Meca, Determination of Very Low Concentration of Bisphenol A in Toys and Baby Pacifiers Using Dispersive Liquid–Liquid Microextraction by In Situ Ionic Liquid Formation and High-Performance Liquid Chromatography, *Pharmaceuticals* 13 (2020)301.

[3] M. Negev, T. Berman, Sh. Reicher, M. Sadeh, R. Ardi, and Y. Shammai, Concentrations of trace metals, phthalates, bisphenol A and flame-retardants in toys and other children's products in Israel, *Chemosphere* 192 (2018) 217-24.

[4] M. Sadeghi, Z. Nematifar, N. Fattahi, M. Pirsaheb, and M. Shamsipur, Determination of bisphenol A in food and environmental samples using combined solid-phase extraction-dispersive liquid-liquid microextraction with solidification of floating organic drop followed by HPLC, *Food Anal*. 9(2016) 1814-24.

[5] S. H. Brandsma, P. E. G. Leonards, J. C. Koekkoek, J. Samsonek, and F. Puype, Migration of hazardous contaminants from WEEE contaminated polymeric toy material by mouthing, *Chemosphere* 294(2022) 133774.

[6] Y. Shi, X. Shan, J. Shao, H. Ye, and S. Tan, Different kinds of methods and mMaterials for determination of bisphenol A in urine and in water, *IOP Conf. Ser. Mater. Sci. Eng.* 612 (2019) 022007.

[7] X. Wu, X. Wang, W. Lu, X. Wang, J. Li, H. You, H. Xiong, and L. Chen, Water-compatible temperature and magnetic dual-responsive molecularly imprinted polymers for recognition and extraction of bisphenol A. J. Chromatogr, *A*. 1435 (2016) 30–8.

[8] V. Samanidou, O. Filippou, E.Marinou, A. Kabir, and K.G. Furton, Sol–gel-graphene-based fabric-phase sorptive extraction for cow and human breast milk sample cleanup for screening bisphenol A and residual dental restorative material before analysis by HPLC with diode array detection, *J Sep. Sci.* 40(2017) 2612-19.

[9] Ch. Li, M. Xiang, and L.Ye, Intercalation behavior and orientation structure of graphene oxide/polyethylene glycol hybrid material, *RSC Adv.* 6 (2016), 72193-200.

[10] S. William, J. Hummers, and R. E. Offeman, Preparation of graphitic oxide, *J. A. Chem. Soc*. 80 (1958) 1339-39.

[11] H. Karimiyan, M. R. Hadjmohammadi, K. L. Kunjali, M. M. Moein, J. Dutta, and M. Abdel-Rehim, Graphene oxide/polyethylene glycol-stick for thin film microextraction of β-blockers from human oral fluid by liquid chromatography-tandem mass spectrometry, *Molecules*. 24(2019) 3664.

[12] A. Kabir, and V. Samanidou, Fabric phase sorptive extraction: A paradigm shift approach in analytical and bioanalytical sample preparation, *Molecules.* 26(2021) 865.

[13] M. Locatelli, A. Tartaglia, H. I. Ulusoy, S. Ulusoy, F. Savini, S. Rossi, F. Santavenere, G. M. Merone, E. Bassotti, C. D'Ovidio, E. Rosato, K.G. Furton, and A. Kabir, Fabric-phase sorptive membrane array as a noninvasive in vivo sampling device for human exposure to different compounds, *Anal. Chem*. 93(2021) 1957–1961.

[14] K. Krishnamoorthy, M. Veerapandian, k. Yun, S. and J. Kim, The chemical and structural analysis of graphene oxide with different degrees of oxidation, *Carbon*. 53(2013)38-49.

[15] Q. Mei, K. Zhang, G. Guan, B. Liu, S. Wang, and Z. Zhang, Highly efficient photoluminescent graphene oxide with tunable surface properties. Chem, *Commun*. 46(2010) 7319-21.

[16] M. Kazempour, H. Namazia, A. Akbarzadeh, and R. Kabiri, Synthesis and characterization of PEG-functionalized graphene oxide as an effective pH-sensitive drug carrier, *Artif. Cells Nanomed. Biotechnol*. 47(2019) 90-94.

[17] Y. Mansourpanah, H. Shahebrahimi, and E. Kolvari, PEG-modified GO nanosheets, a desired additive to increase the rejection and antifouling characteristics of polyamide thin layer membranes, *Chem. Eng. Res. Design*. 104(2015) 530-40.

[18] Y.a Vicente-Martínez, M. Caravaca, and A. Soto-Meca, Determination of Very Low Concentration of Bisphenol A in Toys and Baby Pacifiers Using Dispersive Liquid–Liquid Microextraction by In Situ Ionic Liquid Formation and High-

Performance Liquid Chromatography, *Pharmacy* 13(2020)301.

[19] A. Kabir, R. Mesa, J. Jurmain, and K. G. Furton, Fabric Phase Sorptive Extraction Explained, *Separations* 4(2017) 1-21.

[20] Sh. S. Saini, A. Kabir, A. L. Jagannadha Rao, A. K. Malik, and K. G. Furton, A Novel Protocol to Monitor Trace Levels of Selected Polycyclic Aromatic Hydrocarbons in Environmental Water Using Fabric Phase Sorptive Extraction Followed by High Performance Liquid Chromatography-Fluorescence Detection, *Separations* 22(2017) 1-16.

[21] M. Niu, H. Wang, J. Li, H. Chen, L. Li, H.Yang, X. Liu, Z. Chen, H. Liu, and J. Chen, Polyethylene glycol grafted with carboxylated graphene oxide as a novel interface modifier for polylactic acid/graphene nanocomposites, *R. Soc. Open Sci.* 7(2020) 192154.

[22] V. Shabafrooz, S.R. Bandla, and J. C. Hanan, Graphene/poly(ethylene glycol) dispersions for fabrication of nanocomposites: effects of dispersion processing conditions, *Graphene Technol* 3 (2018) 47-50.

[23] A. Ya'acob, and N. Zainol, Application of central composite design for optimization of microbial growth inhibition using pineapple leaves juice, *IOP Conf. Ser. Mater. Sci. Eng.* 863(2020) 012022.

[24] S. M. Nissy, B. Surendra, K. D. Raju, and M. Vangalapati, Wrenching of Bisphenol A from plastics: Response surface methodology, *Mater Today Proc*.5(2018) 17914.

[25] Gh. Bouazza, M. Assou, E. H. Chatri, and S. Souabi, Optimization by the Response Surface Methodology of Color. 1st International Conference on Innovative Research in Applied Science, *Eng. Technol.* 1*(*2020)1-15.

[26] P. Ghorbannezhad, A. Bay, M. Yolmeh, R. Yadollahi, J. Moghadam, and J. Yazdan Moghadam, Optimization of coagulation–flocculation process for medium density fiberboard (MDF) waste water through response surface methodology, *Desalination Water Treat* 57(2016)1-16.

[27] A. H. Zaibunnisa, S. Norasikin, S. Mamot, and H. Osman, An experimental design approach for the extraction of volatile compounds from turmeric leaves (Curcuma domestica) using pressurized liquid extraction (PLE), *Food Sci. Technol.* 42(2009)233-38.

[28] M. Yolmeh, and S. M. Jafari, Applications of Response Surface Methodology in the Food Industry Processes, *Food Bioproc. Tech*. 10(2017) 413-33.

[29] N. Danbaba, I. Nkama, M. H. Badau, M. N. Ukwungwu, A. T. Maji, M. E. Abo, H. Hauwawu, K. I. Fati, and A. O. Oko, Optimization of Rice Parboiling Process for Optimum Head Rice Yield:

A Response Surface Methodology (RSM) Approach, *Int. J. Agric. For*. 4(2014)154-65.

[30] N. D. Mao, H. Jeong, T. K. N. Nguyen, T. M. L. Nguyen, T. V. V. Do, C. N. Ha Thuc, P. Perré, S. Ch. Ko, H. G. Kim, and D. Th. Tran, Polyethylene glycol functionalized graphene oxide and its influences on properties of poly(lactic acid) biohybrid materials, *Compos. B Eng.* 161(2019) 651-58.

[31] S.N. Alam, N. Sharma, and L. Kumar, Synthesis of Graphene Oxide (GO) by Modified Hummers Method and Its Thermal Reduction to obtain Reduced Graphene Oxide (rGO), *Graphene*. 6(2017)1-18.

[32] G. Venugopal, K. Krishnamoorthy, R. Mohan, and S-J. Kim, An investigation of the electrical transport properties of graphene-oxide thin films, *Mater. Chem. Phys*. 132 (2012) 29-33.

[33] HK. Jeong, MH. Jin, KP. So, SC. Lim, and YH. Lee, Graphene oxide thin film field effect transistors without reduction, *J.Phys. D Appl. Phys*. 42(2009)135109.

[34] H. K. Jeong, YP. Lee, RJWE. L. M. H. Park, KH. An, I. J. Kim, Ch. W. Yang, Ch.Y. Park, R. S. Ruoff, and Y. H. Lee, Evidence of Graphitic AB Stacking Order of Graphite Oxides, *J. Am. Chem. Soc*. 130(2008)1362-66.

[35] K. Krishnamoorthy, M. Veerapandian, k. Yun, and S. J. Kim, The chemical and structural analysis of graphene oxide with different degrees of oxidation, *Carbon* 53(2013) 38-49.

[36] K. K. Selvaraj, G. Shanmugam, S. Sampath, D.G. J. Larsson, and B. R. Ramaswamy, GC-MS determination of bisphenol A and alkylphenol ethoxylates in river water from India and their ecotoxicological risk assessment, *Ecotoxicol. Environ. Saf*. 99(2014)13-20.

[37] Y. Geng, M. Ding, H.Chen, H. F. Li, and J. M Lin, Preparation of hydrophilic carbon-functionalized magnetic microspheres coated with chitosan and application in solid-phase extraction of bisphenol A in aqueous samples, *Talanta* 89 (2012) 189-94.

[38] Y. Su, Ch. Shao, X. Huang, J. Qi, R. Ge, H. Guan, and Z. Lin, Extraction and detection of bisphenol A in human serum and urine by aptamer-functionalized magnetic nanoparticles, *Anal. Bioanal. Chem*. 410(2018) 1885-91.

[39] L. Omer, H. Ahmed, and A. Elbashir, Determination of bisphenol A in exposed bottled water samples to direct sun light using multi walled carbon nanotubes as solid phase extraction sorbent. J. Environ, *Chem. Ecotoxicol*. 8(2016) 51-57.

[40] W. S Kim, A. Do, D. Yeh, and J. Cunningham, Extraction of bisphenol-A and 17β-estradiol from water samples via solid-phase extraction (SPE), *Rev. Anal. Chem.* 33(2014) 59-77.

[41] A. Jurek, and E. Leitner, Analytical determination of bisphenol A (BPA) and bisphenol analogues in

paper products by LC-MS/MS, *Food Addit. Contam. Part A.* 35(2018)2256-69.

تعیین بیس فنول A در نمونه‌های آب معدنی بطری و نمونه‌های اسباب‌بازی با استخراج فاز جذبی پارچه به کمک نانوذرات (NFPSE) و کروماتوگرافی مایع با کارایی بالا

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چکیده

در سال های اخیر وجود بیسفنول A در غذا، آب و اسباب بازی ها به عنوان یک ترکیب سمی در نظر گرفته شده است. در این تحقیق از استخراج فاز جذبی پارچه با استفاده از پوشش نانوکامپوزیت آلی– معدنی به عنوان جاذب برای جداسازی بیس فنول A در نمونه‌های مختلف استفاده شد. بیس فنول A جدا شده توسط کروماتوگرافی مایع با کارایی بالا اندازه گیری شد. پارچه ها با اکسید گرافن عامل دار شده با پلی اتیلن گلیکول (PEG-GO) پوشش داده شدند. شرایط بهینه برای انتخاب نوع پارچه و استخراج بیس فنل A با طرح مرکب مرکزی با ۳ و ۵ متغیر با توجه به روش سطح پاسخ به دست آمد. در ابتدا عوامل موثر در NFPSE مانند نوع پارچه، اتصالات سل–ژل و زمان اتصال بررسی شد. همچنین تاثیر پارامترهای مختلف بر جذب مانند حجم نمونه، زمان جذب، حجم محلول واجذب، زمان واجذب و pH مورد بررسی قرار گرفتند. منحنی کالیبراسیون در منطقه (۰.۱–۱۵ نانوگرم در میلی لیتر) برای بیس فنول A خطی، با ضریب همبستگی بیش از ۹۹ درصد بود. حد تشخیص (LODs) و حد کمی به ترتیب ۰.۱۱ نانوگرم در میلی لیتر و ۰.۳۷ نانوگرم در میلی لیتر بود. تکرارپذیری (RSD) با سه آزمایش تکراری ۱.۲۵ درصد بود. بازیابی برای نمونه های مختلف در محدوده ۹۵ تا ۹۷ درصد به دست آمد. با توجه به نتایج به دست آمده، روش ذکر شده در این تحقیق را می توان به عنوان روشی تکرارپذیر با ظرفیت جذب بالا برای تعیین بیس فنول A در آب های معدنی داخل بطری و اسباب بازی ها معرفی کرد.

کلید واژه ها

نانوذرات؛ استخراج جذبی فاز پارچه؛ بیسفنولA؛ سل–ژل؛ گرافن اکسید–پلی اتیلن گلیکول