JCHR (2022) 12(1), 81-91

Journal of Chemical Health Risks

www.jchr.org

ORIGINAL ARTICLE

The Synthesis of Surfactant Coated Glass Foam to Extract and Determine Trace Quantities of Polycyclic Aromatic Hydrocarbons in Drinking Water

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(Received: 17 February 2021 Accepted: 12 June 2021)

KEYWORDS

Glass foam;
PAHs determination;
Extraction;
CTAB surfactant

ABSTRACT: The present work deals with a simple, inexpensive, sensitive, high performance and economic technique for extracting and preconcentrating trace quantity of PAHs compounds through glass foam modified with CTAB surfactant. Solution desorption was employed subsequently for transferring the extracted PAHs into a gas chromatography-mass spectrometry's injection port. BET, TGA, and FT-IR were used to characterize glass foam and CTAB/glass foam. Operative parameters in PAHs extraction and preconcentration such as amount of sorbent, pH, recovery solvent type, ionic power of solution, contacting time, and recovery time were enhanced to quantitatively determine PAHs. Analytical statistics of merit including limit of detection, accuracy, and linear range were determined to prove the suitability of our suggested technique. The CTAB/glass foam represented higher sensitivity to detect very lower concentration of PAHs such as phenanthrene, fluorene, pyrene and anthracene at ng mL^{-1} level with high accuracy for drinking water samples.

INTRODUCTION

Water as the vital material to sustain life on the earth is mainly contaminated by industrial wastes and municipal sewage discharges [1, 2]. The industrial wastes are particularly comprise various toxic substances severely polluting clean water sources. They impose serious threats to the human health with their extremely poisonous constituents such as polycyclic aromatic hydrocarbons (PAHs) [3]. PAHs are a main group of ubiquitous environmental organic micropollutants with fused aromatic groups. They are created over the fossil fuels incomplete combustion [4]. They exist in the soils of industrially polluted sites at higher concentrations due to their lipophilic nature [5]. Hence, they contaminate water sources while threatening human health [6]. They have weak water solubility (μg L^{-1}), hence, they exist in water sources concentrations of at ng L^{-1} [7]. Even such lower PAHs levels with consistent exposure may result in accumulation in tissues [8] causing detrimental impacts to the human health. PAHs experiences metabolic activation in body via cytochrome P450 enzymes [9]. Moreover, they

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DOI: 10.22034/jchr.2021.1923819.1266

can pass cell membrane barriers through lipophilicity while reacting with the cellular DNA [10], creating PAH−DNA adducts as the first stage of carcinogenesis [11]. The body possesses its own protection control for the proofreading enzyme even though DNA polymerase occasionally cannot correct such errors during DNA replications for repairing DNA harms. Therefore, 17 PAH was classified by the Agency for Toxic Substances and Disease Registry (ATSDR) as the largest concern regarding the adverse health and potential exposure impacts on humans [12]. The eight PAHs denoted are also involved within ATSDR-PAH as identified carcinogens by European Union, in the regulation European Commission (EC)’s annex VI [13]. Another list was completed by the USA Environmental Protection Agency (EPA) with 16 priority compounds called 16 EPA-PAH oriented by potential toxicity for frequency of occurrence or human exposure at risky waste sites. Such compounds include naphthalene, acenaphthene, acenaphthylene, phenanthrene, fluorene, fluoranthene, benzo (a) anthracene, anthracene, pyrene, benzo (b) fluoranthene, chrysene, benzo (a) pyrene, benzo (g,h,i) perylene, abenzo (k) fluoranthene, nd dibenz (a,h) anthracene. This list is often regarded as a reference in environmental sample assessment [14, 15]. Considering the significant impacts of PAHs compounds, it is vital to discover a sensitive analytical technique to determine PAHs in drinking water samples. By determining PAHs compounds in real samples like tap water from Qaemshahr and Gorgan, these toxic pollutants can be controlled or their presence can be minimized in water sources, mainly in the drinking water sources. Numerous analytical techniques have been discovered for this purpose so far, such as integrating gas chromatography-mass spectrometry (GC–MS) and ultrasonic extraction [16], jet-cooled laser-induced fluorescence [17], SPME-GC-MS [18], combustion of ultrasonic extraction and fluorescence spectroscopy [19], combination of soxhlet extraction with GC–MS [20, 21] and high performance liquid chromatography [22, 23]. In numerous cases, it is quite difficult to determine PAHs compounds in drinking water for both the lower levels of this compound in the specimens and the higher sample matrices complexity. Thus, to determine PAHs, a method is often required presenting lower detection limits. Though GC-MS approaches are powerful analytical instruments to determine trace quantities of PAHs compounds in drinking water, preconcentration methods integrated with GC-MS are still essential. Normally, preconcentration is essential prior to instrumental analysis. Some preconcentration and extraction approaches have been used to extract organic substances, among which are liquid–liquid extraction [24], cloud point extraction [25], solid-phase extraction (SPE) [26-28], and potentiometric methods [29-31]. Though, some of preconcentration approaches possess the drawbacks including high cost, complex operation, time consuming separation process, and large quantities of toxic organic solvents. SPE methods have been utilized in PAHs investigation as a result of higher sensitivity, good, quick stability, low cost equipment, simple operation, and extensive dynamic range [32]. In general, SPE process is employed for this objective since it has higher concentration factor, simplicity, rapidity, and the possibility of its integration with different analytical approaches [33]. A higher surface area is required in SPE, therefore, various kinds of sorbents can be prolonged to extract and preconcentrate. Glass foam is used as a sorbent in SPE method due to its low price, which is economical, as well as its high surface area. This glass structure has a unique combination of ideal physical properties and has a wide working temperature range that allows the use of glass foam in a wide variety of conditions and also has very good compatibility with the environment and very high stability. These years a huge deal of interest has been attratced to modify the adsorbent’s surface [34]. In this work, we used glass foam coated with cetyltrimethylammonium bromide (CTAB) surfactant, as a positive sorbent, to extract and separate PAHs compounds such as fluorene, phenanthrene, anthracene and pyrene. Glass foam coated with CTAB can be increasing adsorption capacity, and extraction efficiency. Consequently, PAHs compounds were determined in drinking water specimens through GC-MS.

MATERIALS AND METHODS

Reagents and apparatus

Fluorene, phenanthrene, anthracene and pyrene standards were obtained from Sigma-Aldrich and distilled before use. The stock solution of such compounds was made in acetone at concentration of 1 mg mL^{-1}. To prepare the working solution of above compounds each weak, the stock solution was diluted with double distilled water. CTAB surfactant was attained from Fluka (Buchs, Switzerland). Glass foam was obtained from Azar-jaam company (Amol, Iran). All solvents utilized in this work had analytical reagent grade or HPLC grade.

To quantitatively determine, a gas chromatograph model Hewlett-Packard (HP, Palo Alta, USA) HP 6890 series GC armed with a split/splitless injector was used along with HP 5973 mass-selective detector systems. The MS acted in the EI mode (70 eV). The carrier gas was Helium (99.999%) with the flow rate of 1 mL min^{-1}. To separate PAHs, a 60 m×0.25 mm HP-5 MS column was used (thickness of 1 μm film). For 2 min, the column was kept at 70 °C, then incremented to 140 °C at a rate of 15 °C/min. It was maintained at this temperature for 3 minutes. The injector temperature was adjusted at 250 °C and all injections were oriented by the split mode and the split ratio of 5:1. The GC-MS interface was kept at 280 °C. Evaluation of the surface area was accomplished by BET method using Quanta chrome, Chem BET 300 TPR/TPD. The chemical structures' products were assessed with Fourier transform infrared spectroscopy (FT-IR) (Shimadzu model 4100, Japan).

Modification of the CTAB/glass foam

2.0 g of glass foam was inserted to $NaHCO_3$ 0.16 M (25 mL) and transferred into a 100 mL beaker. The solution was then stirred for 20 minutes by a shaker until mixing the glass foam with $NaHCO_3$. Centrifuging the solution was performed for 5 minutes at a speed of 4000 rpm. The glass foam was rinsed with distilled water twice at the bottom by upper solution overflow. Adding 1.0 g of CTAB to 25 mL distilled water in a container, the mixture was put into centrifuge tube while stirring for 120 minutes via a shaker. It was centrifuged for 15 minutes. Based on tube overflow upper solution, the centrifuging tube was located in an oven at 60 °C to dry and transform to powder (Figure 1).

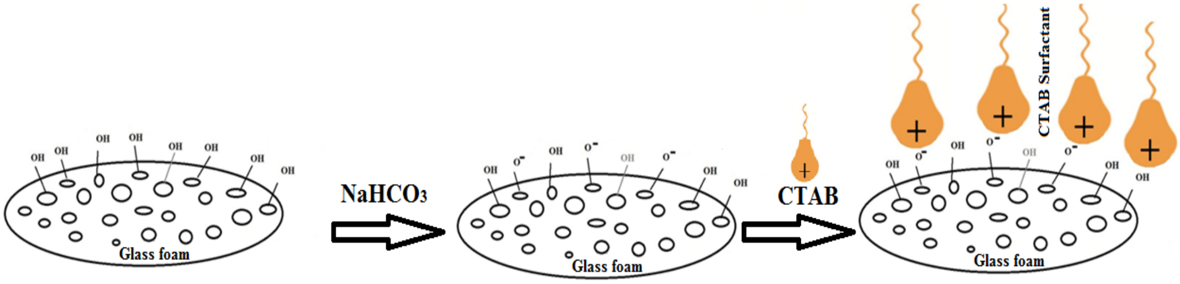

Figure 1. Preparation of CTAB/Glass foam

General extraction process

Preparing 10 mL of PAHs solution (100 ng mL^{-1}), the pH value was set by addition of ammonium buffer solution (0.3 M, pH 9.0), then 0. 4 g of modified glass foam was inserted to 10 mL of solution while stirring for 20 min by a shaker at room temperature. Followed by centrifuging the mixture (at 5000 rpm for 10 min) eluting the PAHs retained on sorbent was performed with 1.0 mL acetone. Ultimately, PAHs compounds were defined by GC-MS after stirring for 15 min via a shaker and centrifuging the solution.

RESULTS AND DISCUSSION

Characterization of the glass foam and CTAB/glass foam

BET analysis for glass foam indicated that the specific surface area of glass foam is 54.6 m^2/g that decreases to 47.9 m^2/g after surface modifications. In the discussed process, extraction and separation of PAHs in this work is oriented by solid phase extraction method by the adsorption over the active sites of modified glass foam so, high surface area and porous structure are auspicious parameters for the better adsorption. In this survey, the details of BET for the prepared glass foam shows high specific surface area.

TGA analysis of the specimens is represented in figures 2a, and b. Amount of weight loss for the glass foam alone (Figure 2a) in the range of 25-800 °C is 5.68% that indicates the thermal stability of the glass foam up to 800 °C. TGA analysis for the modified glass foam (Figure 2b) exhibit a large weight losses. This observes between 220 and 270 ^{o}C in order to decomposition of CTAB surfactant in the modified glass foam. As a result, TGA analysis shows how much surfactant is sitting on the adsorbent and also shows the degree of thermal stability of the adsorbent.

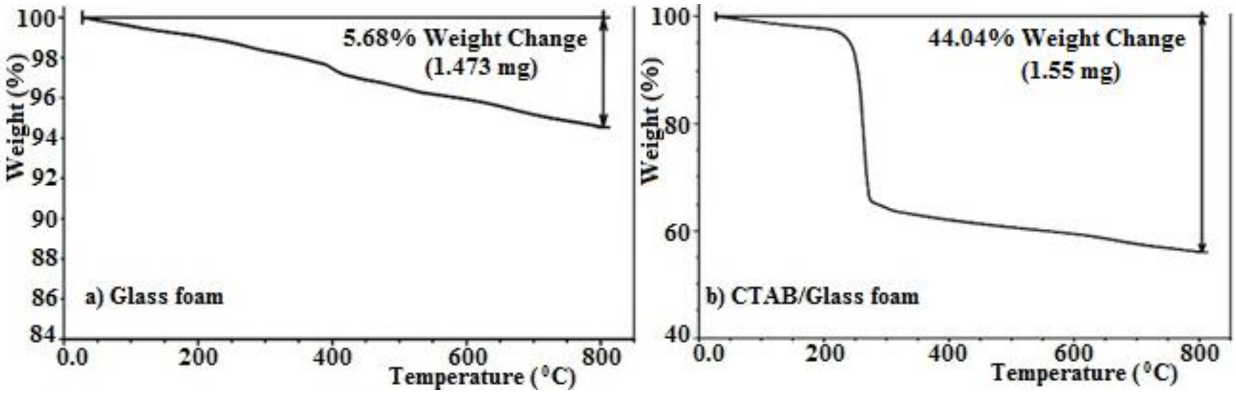

Figure 2. TGA analysis curve for glass foam (a) and CTAB/glass foam (b)

Fourier transmission infrared spectroscopy (FT-IR) was utilized to verify the linkage between glass foam and the CTAB surfactant as shown in Figs.3a and b. The comparing the FT-IR spectrum of glass foam alone and glass foam coated with CTAB represents important results for identifying the groups substitution. The FT-IR spectrum of glass foam (Figure 3a) identified the peaks of O-H group at 3445 cm^{-1}, Si-O bond (stretching vibration) at 1092 cm^{-1} and Si-O bond at 453 cm^{-1} (bending vibration), respectively. In the FT-IR spectra of CTAB/glass foam (Figure 3b), appeared the peaks of C-H bond (stretching vibration) at 2930 cm^{-1}, C-H bond (bending vibration) at 1465 cm^{-1} and C-N bond at 1071 cm^{-1} (bending vibration), respectively. Such vibrations indicate that CTAB surfactant has been immobilized successfully onto the glass foam surface.

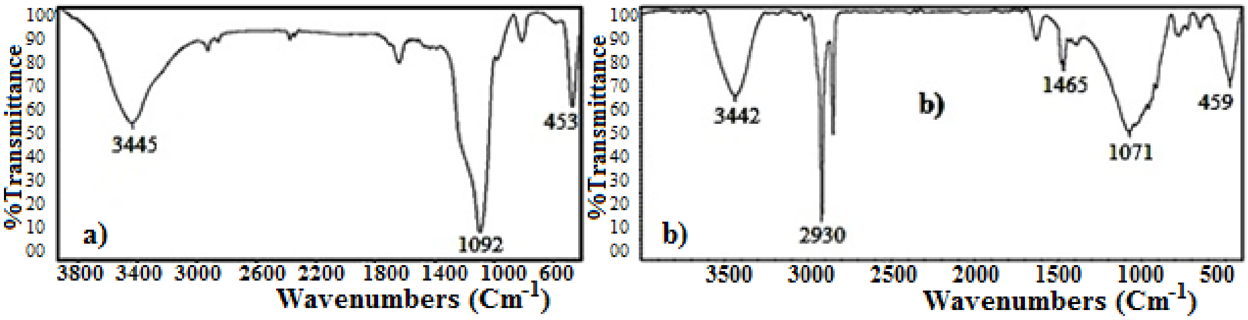

Figure 3. Infrared spectra of glass foam (a) and CTAB/glass foam (b)

Optimization of the extraction stage

The pH effect on the efficiency of extraction

The solution's pH value is one of the most significant factors influencing the adsorption performance of PAHs on adsorbents. The reason is the sorbents' surface structure and the interaction between PAHs and sorbents. The effects of pH on recovery of PAHs in the pH range of 2 to 10 was examined (maintaining the other parameters fixed). The maximum percent detections were in pH=9 (>96%) (Fig 4). This result reveals that the absorption of PAHs happened in this pH. CTAB/glass foam was protonated at lower pH values, therefore, pH= 9 was chosen as the best pH.

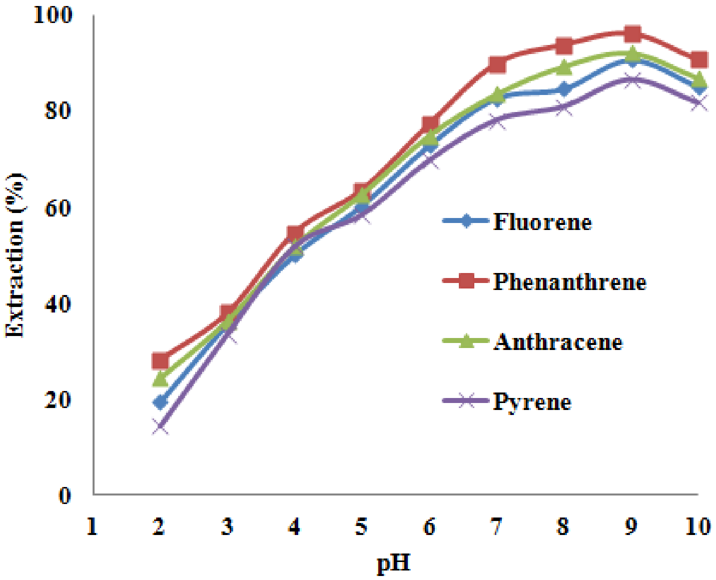

Figure 4. The effects of pH on the modified glass foam activity. sample volume, 10 mL; quantity of sorbent, 0.4 g ; recovery solvent, 1.0 mL acetone; extraction time, 20 min; C_{PAHs}, 100 ng mL^{-1}

Extraction time effects on the efficacy of extraction

A direct association is found between the extraction time and the extracted quantity. Optimal extraction time was defined by altering the contact time between 5 and 40 min. The extraction time profiles for the calculated PAHs compounds from aquatic specimens are represented in Figure 5. Almost for all compounds, only a small increment was found in the response followed by the initial 20 min. To shorten the analysis time, an extraction time of 20 min was chosen.

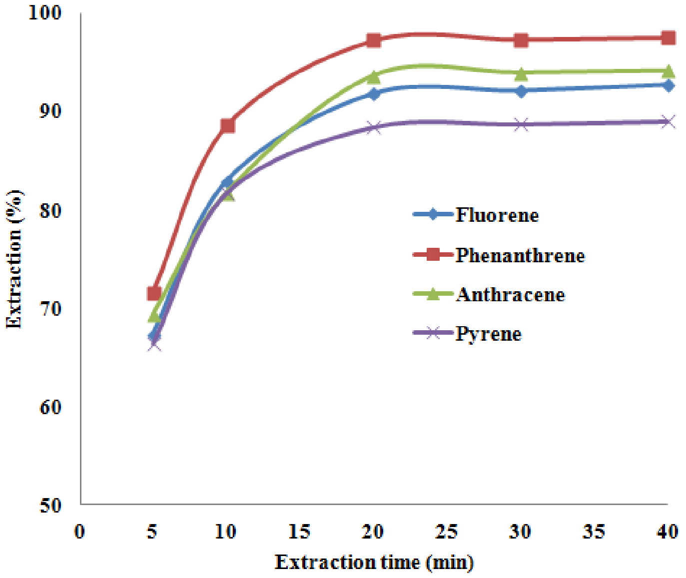

Figure 5. Extraction time profiles of PAHs from aqueous samples. sample volume, 10 mL; quantity of sorbent, 0.4 g ; recovery solvent, 1.0 mL acetone; pH value, 9.0; C_{PAHs}, 100 ng mL^{-1}

Effects of the amount of CTAB/glass foam

The effect of different quantities of sorbent (CTAB/glass foam) was assessed within the range of 0.1 to 0.5 g (Fig. 6). The results revealed that with incrementing in the amount of CTAB/glass foam, the extraction of PAHs compounds increased and reached a constant value when the amount of CTAB/glass foam reaches to 0.4 g. Hence, 0.4 g of sorbent was chosen for further studies.

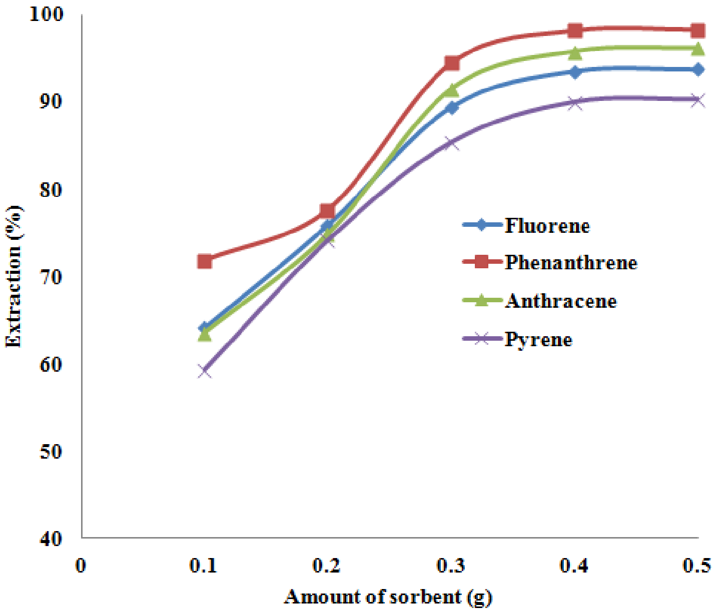

Figure 6. The effects of sorbent quantity on the extraction. The sample volume, 10 mL; pH value, 9.0; extraction time, 20 min; recovery solvent, 1.0 mL acetone; C_{PAHs}, 100 ng mL^{-1}.

The effects of ionic strength

Aqueous solubility decreases with incrementing ionic strength for numerous organic analytes. Hence, the partitioning from the aqueous solution to the coating is enhanced. An inorganic salt is normally inserted to the aqueous matrix to increase the ionic strength. The effect of ionic strength was assessed by addition of various quantities of sodium chloride within the range of 0.01 to 0.05 M, for which the results are presented in Fig. 7. At a salt concentration higher than 0.03 M, the responses for all analytes are constant approximately. About 0.03 sodium chloride was utilized as the optimal quantity for the subsequent works.

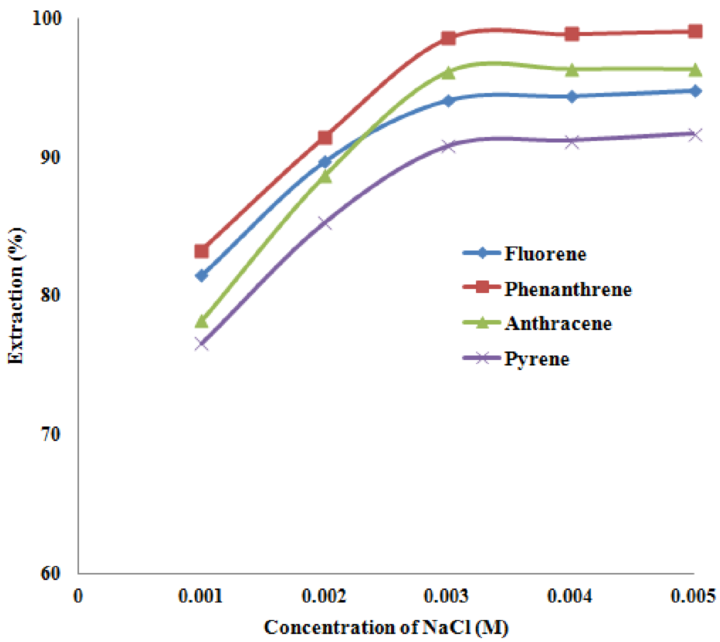

Figure 7. Effect of salt addition on the extraction efficiency. sample volume, 10 mL; pH value, 9.0; amount of sorbent, 0.4 g; extraction time, 20 min; recovery solvent, 1.0 mL acetone; C_{PAHs}, 100 ng mL^{-1}.

Selection of recovery solvent

Different experiments were utilized for selecting a proper solvent to desorb PAHs from the modified glass foam. The PAHs compounds were desorbed with 1.0 mL of diverse solvents such as methanol, hexane, acetone and toluene. According to Figure 8, using 1.0 mL of acetone could affect quantitative desorption of PAHs from the modified glass foam. Hence, we selected 1.0 mL of acetone as solvent for desorption of the PAHs.

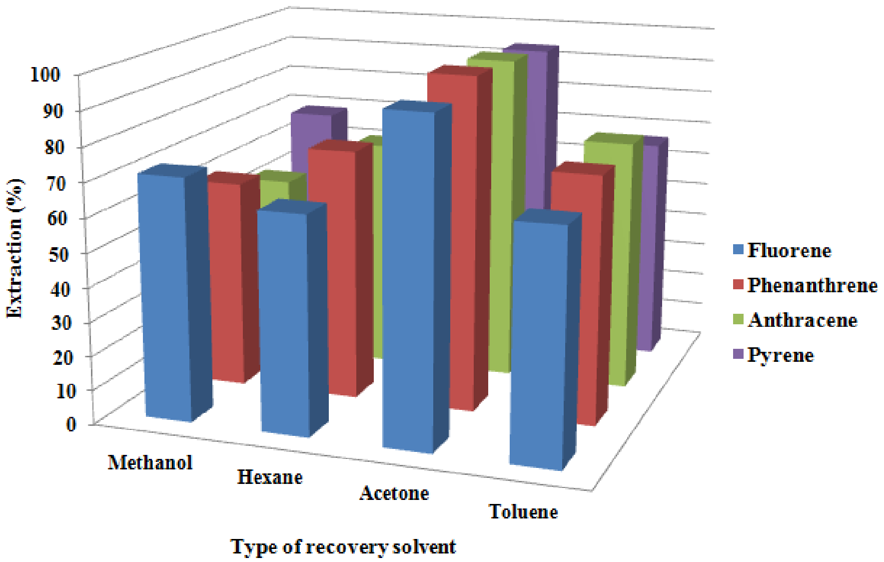

Figure 8. The impacts of solvent kind on the recovery of PAHs. The sample volume, 10 mL; pH value, 9.0; amount of sorbent, 0.4 g; extraction time, 20 min; C_{PAHs}, 100 ng mL^{-1}.

Effect of recovery time

Other important factor affecting the preconcentration process is time of recovery by solvent utilized for the extraction of PAHs from the sorbent. An appropriate time should be used to achieve a higher enrichment factor. Various times were utilized for further extraction optimum time. The findings revealed that 15 min is the best time for desorption of the PAHs. (Figure 9).

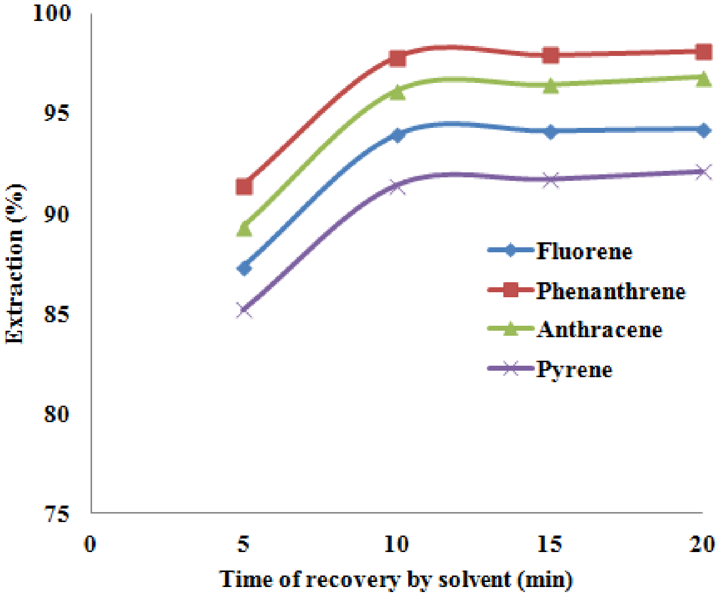

Figure 9. Effect of time of recovery by solvent on the extraction efficiency. The sample volume (10 mL); pH value (9.0); amount of sorbent (0.4 g); extraction time, 20 min; recovery solvent, 1.0 mL acetone; C_{PAHs}, 100 ng mL^{-1}.

Determining characteristics of the analytical technique

Plotting the calibration curves for each PAH, the ratio was calculated between chromatographic areas for every target compounds associated with the equivalent internal standard area (A_s/A_{is}) against quantity in ng of PAH standard utilized to calibarte the quantity in ng of the specific internal standard (m_s/m_{is}). The calibration curves were built based on the analytical reasons and considering the extensive concentration range where PAH exist in the samples utilizing 8 concentration levels each in triplicate. The correlation coefficients (R^2) of 0.984-0.996 are represented by linear fitting of resultant calibration curves for every compound. Table 1 represents these coefficients along with linear range (2–1000 ng mL^{-1} in all the cases) as well as the main analytical features. It is indicated that quantitative data can be acquired confidently within the analysis range. The quantity of PAH in the target specimens is determined based on the supplementary material and further verifications to check the accurate calibration of each PAH curve in terms of EPA for toxic organic air pollutants [33]. The limit of detection ($LOD_{Fluorene}$ =3.2 ng mL^{-1}, $LOD_{Phenanthrene}$ =0.7 ng mL^{-1}, $LOD_{Anthracene}$ =0.9 ng mL^{-1} and LOD_{Pyrene} =1.8 ng mL^{-1}) was determined as $3S_b/m$ (m: slope of calibration curve after preconcentration; S_b: standard deviation of the blank signals). Preconcentration factor (PF) determined as the ratio of sample volume (10 mL) to eluent volume (1.0 mL) is 10. The precision was presented as the percentage of the relative standard deviation (%RSD) representing the accuracy of the proposed method. The values for the three different concentrations of PAHs compounds were ranged from 1.1-2.6%.

Table 1. Analytical features of the presented technique for PAHs determination

PAHs	RSD	Linear range (ng mL^{-1})	Detection limit (ng mL^{-1})	Correlation coefficient (R^2)
Fluorene	2.3	10-1000	3.2	0.984
Phenanthrene	1.1	2-1000	0.7	0.992
Anthracene	1.8	3-1000	0.9	0.996
Pyrene	2.6	5-1000	1.8	0.988

Analysis of drinking water samples

The discussed above optimized method was utilized for determining PAHs compounds of drinking water specimens including tap water from Qaemshahr and Gorgan. Hence, the samples (10 mL) were preconcentrated via modified composites based on the proposed technique. Table 2 confirms the capability of the presented technique to determine the PAHs compounds in the real specimens.

Table 2. Determining PAHs in drinking and spiked water samples

PAHs	Sample (drinking water)	PAHs spiked (ng mL^{-1})	PAHs detected (ng mL^{-1})	Relative Recovery (%)
Fluoren	Qaemshahr	_	N.D.[a]	–
		50	48.7 (2.9)[b]	97.4
	Gorgan	_	N.D.	–
		50	47.6 (3.1)	95.2
Phenanthrene	Qaemshahr	_	N.D.	–
		50	50.2 (2.6)	100.4
	Gorgan	_	N.D.	–
		50	48.2 (1.8)	96.4
Anthracene	Qaemshahr	_	N.D.	–
		50	47.9 (2.3)	95.8
	Gorgan	_	N.D.	–
		50	48.3 (1.7)	96.6
Pyrene	Qaemshahr	_	N.D.	–
		50	50.3 (2.6)	100.6
	Gorgan	_	N.D.	–
		50	48.4 (3.2)	96.8

[a]Not detected; [b]RSD of three replicate experiments

CONCLUSIONS

In this work, a sorbent was obtained by coating of glass foam with CTAB surfactant by a straightforward and easy modification technique. The functionalization glass foam with CTAB surfactant as anew sorbent is shown to be highly efficient to preconcentration and extraction of PAHs in laboratory and real aqueous samples. It was revealed that the PAHs adsorption strongly affect the surfactant's electronic structure. SPE method was used because of the great chemical and thermal strength large surface area, and sorbent's good presentation. This approach has benefits attributed to the reproducible results, less utilization of organic solvents, fewer technical aids, high speed, extraction cleaner, and small costs. Utilizing the suggested sorbent increased the adsorption capacity as a result of the PAHs representing lower resistance against mass transition that are adsorbed rapidly. Utilizing GC-MS indicated that sorbent is very selective and sensitive to detect lower concentrations of PAHs compounds. It also has a good accuracy in analysis of real specimen. The method suggested by SPE has smaller RSD, appropriate limit of detection and linear range. The proposed technique was satisfactory proven to determine the PAHs in drinking water specimens at ng mL^{-1} levels.

Data availability

The raw/processed information needed for reproducing such results cannot be shared since the data are also a part of an ongoing work.

ACKNOWLEDGEMENTS

The authors of article thank from financial support of research and technology sincerely of Qaemshahr branch, Islamic Azad University

Conflict of interest

The researchers declared no conflict of interest.

REFERENCES

1. Reemtsma T., Weiss S., Mueller J., Petrovic M.,Gonzalez S., Barcelo D., Ventura F. Knepper T.P., 2006. Polar Pollutants Entry into the Water Cycle by Municipal Wastewater: A European Perspective. Environ Sci Technol. 40, 5451−5458.

2. Sonune A., Ghate R., 2004. Developments in wastewater treatment methods. Desalination. 167, 55−63.

3. Sanchez-Avila J., Bonet J., Velasco G., Lacorte S., 2009. Determination and occurrence of phthalates, alkyl phenols, bisphenol A, PBDEs, PCB sand PAHs in an industrial sewage grid discharging to a Municipal Wastewater Treatment Plant. Sci Total Environ. 407, 4157−4167.

4. Behera B.K., Das A., Sarkar D.J., Weerathunge P., Parida P.K., Das B.K., Thavamani P., Ramanathan R., Bansal V., 2018. Polycyclic aromatic hydrocarbons (PAHs) in inland aquatic ecosystems: Perils and remedies through biosensors and bioremediation. Environ Pollut. 241, 212−233.

5. Tsibart A.S., Gennadiev A.N., 2013. Polycyclic aromatic hydrocarbons in soils: Sources, behavior, and indication significance (a review). Eurasian Soil Sci. 46, 728−741.

6. Wilson S.C., Jones K.C., 1993. Bioremediation of soil contaminated with poly nuclear aromatic hydrocarbons (PAHs): A review Environ Pollut. 81, 229−249.

7.Sun C., Zhang J., Ma Q., Chen Y., Ju H., 2017. Polycyclic aromatic hydrocarbons (PAHs) in water and sediment from a river basin: sediment water partitioning, source identification and environmental health risk assessment. Environ Geochem Health. 39, 63−74.

8. Nwaichi E.O., Ntorgbo S.A., 2016. Assessment of PAHs levels in some fish and seafood from different coastal waters in the Niger Delta. Toxicol Rep. 3, 167−172.

9. Shimada T., Fujii-Kuriyama Y., 2004. Metabolic activation of polycyclic aromatic hydrocarbons to carcinogens by cytochromes P450 1A1 and 1B1.Cancer Sci. 95, 1−6.

10. Plant A.L., Knapp R.D., Smith L.C., 1987. Mechanism and rate of permeation of cells by polycyclic aromatic hydrocarbons. J Biol Chem. 262, 2514−2519.

11. Pratt M.M., John K., MacLean A.B., Afework S., Phillips D.H., Poirier M.C., 2011. Polycyclic aromatic hydrocarbon (PAH) exposure and DNA adduct semi-quantitation in archived human tissues. Int J Environ Res Public Health. 8, 2675−2691.

12. Agency for Toxic Substances and Disease Registry, ATSDR. Toxicological profile for polycyclic aromatic hydrocarbons. Atlanta; 1995.

13. Federal Institute for Risk Assessment, BfR. Carcinogenic polycyclic aromatic hydrocarbons (PAHs) in consumer products to be regulated by the EU-risk assessment by BfR in the context of a restriction proposal under REACH, Opinion Nr. 032/2010. Berlin, German. 2010.

14. Ballesteros R., Hernandez J.J., Lyons L.L., 2010. An experimental study of the influence of bio fuel origin on particle-associated. Atmos Environ. 44, 930–8.

15. Song YF., Jing X., Fleischmann S., Wilke B.M., 2002. Comparative study of extraction for determination of PAH from contaminated soils and sediments. Chemosphere. 48, 993–1001.

16. Rissanen T., Hyotylainen T., Kallio M., Kronholm J., Kulmala M., Riekkola M.L., 2006. Characterization of

organic compounds in aerosol particles from a coniferousforest by GC–MS. Chemosphere. 64, 1185–95.

17. Wartel M., Pauwels J.F., Desgroux P., Mercier X., 2010. Quantitative measurement of naphthalene in low-pressure flames by jet-cooled laser-induced fluorescence. Appl Phys B. 100, 933–43.

18. Ballesteros R., Hernandez J.J., Lyons L.L., 2009. Determination of PAHs in diesel particulate matter using thermal extraction and solid phase micro-extraction. Atmos Environ. 43, 655–62.

19. Mastral A., Callen M., Murillo R., Garcia T., Vinas M., 1999. Influence on PAH emissions of the air flow in AFB coal combustion. Fuel. 78, 1553–7.

20. Aracil I., Font R., Conesa J.A., 2005. Semivolatile and volatile compound from the pyrolysis and combustion of polyvinyl chloride. J Anal Appl Pyrol. 74, 465–78.

21. Font R., Aracil I., Fullana A., Martin-Gullon I., Conesa J.A., 2003. Semivolatile compounds in pyrolysis of polyethylene. J Anal Appl Pyrol. 69, 599–611.

22. Ledesma E.B., Marsh N.D., Sandrowitz A.K., Wornat M.J., 2002. Global kinetic rate parameters for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of catechol, a model compound representative of solid fuel moieties. Energy Fuel. 16, 1331–6.

23. Thomas S., Ledesma E.B., Wornat M.J., 2007. The effects of oxygen on the yields of thethermal decomposition products of catechol under pyrolysis and fuel rich oxidation conditions. Fuel. 86, 2581–95.

24. Mirabi A., Jamali M.R., Kazemi Q., 2016. Determination of trace amounts of manganese in water samples by flame atomic absorption spectrometry after dispersive liquid-liquid microextraction, Bulg Chem Commun. 48, 525-531.

25. Movaghgharnezhad Sh., Mirabi A., Toosi M.R., Shokuhi-Rad A., 2020. Synthesis of cellulose nanofibers functionalized by dithiooxamide for preconcentration and determination of trace amounts of Cd (II) ions in water samples, Cellulose. 27, 8885–8898.

26. Mirabi A., Dalirandeh Z., Shokuhi-Rad A., 2015. Preparation of modified magnetic nanoparticles as asorbent for the preconcentration and determination of cadmium ions in food and environmental water samples prior to flame atomic absorption spectrometry. J Magn Magn Mater. 381, 138-144.

27. Mirabi A., Shokouhi-Rad A., Nourani S., 2015. Application of Modified Magnetic Nanoparticles as a Sorbent for Preconcentration and Determination of Nickel Ions in Food and Environmental Water Samples. Trends Anal Chem. 74, 146-151.

28. Mirabi A., Shokuhi-Rad A., Jamali M.R., Danesh N., 2016. Use of Modified γ-Alumina Nanoparticles for the Extraction and Preconcentration of Trace Amounts of Cadmium Ions. Aust J Chem. 69, 314–318.

29. Li X.G., Feng H., Huang M.R., Gu G.L., Moloney M.G., 2012. Ultrasensitive Pb (II) potentiometric sensor based on copolyaniline nanoparticles in a plasticizer-free membrane with a long lifetime. Anal Chem. 84, 134-140.

30. Huang M.R., Ding Y.B., Li X.G., Liu Y., Xi K., Gao C.L., Kumar R.V., 2014. Synthesis of semiconducting polymer microparticles as solid ionophore with abundant complexing sites for long-life Pb(II) sensors, ACS appl mater interfaces. 6, 22096-22107.

31. Huang M.R., Ding Y.B., Li X.G., 2013. Lead ion potentiometric sensor based on electrically conducting microparticles of sulfonic phenylenediamine copolymer. Analyst. 138, 3820-3829.

32. Lam S.H., Chen C.K., Wang J.Sh., Lee Sh.Sh., 2008. Investigation of Flavonoid Glycosides from Neolitsea sericea var. auratavia the General Method and HPLC-SPE-NMR. J Chin Chem Soc. 55, 449-455.

33. Ghaedi M., Shokrollahi A., Ahmadi F., 2007. Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame aomic absorption spectrometry. J Hazard Mater. 142, 272-278.

34. Mirabi A., Shokuhi-Rad A., Khodadad H., 2015. Modified surface based on magnetic nanocomposite of dithiooxamide /Fe_3O_4 as a sorbent for preconcentration and determination of trace amounts of copper. J Magn Magn Mater. 389, 130-135.

35. Environmental Protection Agency, EPA. Compendium of methods for the determination of toxic organic compounds in ambient air, method TO-13A, EPA/625/R-96/010b. Ohio. 1999.