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A Validated SPE-UPLC-DAD Method for Quantification of Parabens in Industrial Waste Effluent Water Samples by Using Activated Carbon Nanofiber Modified Filter Paper

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The present work describes a sensitive, simple, cost-effective and fast analytical procedure to detect the parabens in industrial waste effluent water samples using novel activated carbon nanofiber (CNF) modified filter paper based solid phase extraction technique coupled with liquid chromatography with photodiode array detector (UPLC-PDA). The carbon nanofiber coated filter paper was used as an adsorbent and also characterized by field emission scanning electron microscope (FESEM) showed superior porous structure. Various factors effecting the adsorption and desorption process were studied. The optimum parameters which improve the efficiency are paper length 1 cm × 2 cm, adsorption time 15 min, eluent methanol, eluent volume 5 mL, sample pH 7, desorption time 2 min, 2% salt addition and 300 rpm stirring rate respectively. The parabens exhibited superior linearity ranging from 0.1-50 ng mL^{-1}. The regression coefficient (R^2) value ranging from 0.9981-0.9989. This method exhibited good sensitivity with the quantification limit (LOQ) between 0.5-0.75 ng mL^{-1} and detection limit (LOD) over the range of 0.1-0.25 ng mL^{-1}. The precision was expressed from the RSDs values from 0.74-0.97 %. The spiked analytes revealed excellent recoveries in the range of 95.30-116.72 % with RSD less than 5.72 % for all the water samples also applied for real samples.

Keywords: Carbon nanofiber, Dispersion, Effluent water, Parabens, UPLC-DAD.

INTRODUCTION

In recent years, people are living in an environment where they are forced to use some artificial environmental chemicals and numerous studies have been reported the possible risky effects such as disruption of the endocrine system resulting in malignant melanomas development and breast cancers, hormonal control problems in humans, metabolic disorders and many other health problems [1-6]. In particular, *p*-hydroxybenzoic acid alkyl esters (parabens) such as butylparaben, propylparaben, ethylparaben and methylparaben, which are extensively used as artificial preservatives in foodstuffs, pharmaceuticals, paints and personal beauty products due to their excellent antifungal and antimicrobial behaviour. Mostly, parabens are used and deliberated as preservatives because it prevents microbial growth in pharmaceutical products and edible items [7,8]. Since parabens has numerous applications in consumer products, a huge quantity has been discarded out into the industrial and domestic water bodies. Also, several reports concerned with contamination of industrial effluent waters by parabens and at lesser levels in effluents has led to their appearance in industrial effluent water. Subsequently, parabens are reflected as emerging pollutants, due to demand of these chemicals for varied pervasive applications which can cause potential harmful effects in humans have gathered the attention among many researchers valuing the human benefits [9-14].

The pre-concentration is essential for the analysis of biological and environmental samples because of the very low levels of target analytes anticipated in it. Various extraction methods have been proposed to investigate parabens from different complex matrices which includes molecularly imprinted polymers for solid phase extraction (MISPE), solid phase extraction (SPE), ultrasound-assisted dispersive liquid-liquid microextraction (UA-DLLME), stir-bar sorptive extraction (SBSE), dispersive liquid-liquid microextraction (DLLME) solidified oating vesicular coacervative drop micro-extraction (SFVC-

DME) [9,15-20]. All these methods have some drawbacks like laborious, time-dependent, possess low sensitivity, sorbent preparation for traditional SPE is difficult and tedious. Therefore, the researchers pay much attention in developing facile, efficient, fast and eco-friendly material fabrication techniques for the parabens determination in various aquatic systems.

Now, many methods have been introduced for the extraction of the several toxic compounds in different media by utilizing paper-based solid phase extraction (P-SPE) with high enrichment factors [21,22]. For analysis of water and food samples, microfluidic paper-based analytical devices (μPADs) were utilized where a paper is considered as a main substrate [23]. In view of the sample extraction context, cost-effective and disposable substrates can be fabricated using a paper which can be used in planar microextraction techniques [24,25]. To extend the application feature, paper must be improved by the in-surface chemical coating using a sorptive phase or by simply coating physically with a liquid phase [26]. Paper is an environment friendly because it is biodegradable and can be disposed easily by incineration; in addition to that, it is a cheap material with high availability. With numerous advantages like easy degradation after usage, low cost and easy manipulation, P-SPE materials are used widely. Considering these facts like applications and advantages of paper-based SPE technique, a facile and highly selective carbon nanofiber coated filter paper based SPE combined with ultra-high performance liquid chromatography technique is employed for the extraction of various parabens from industrial effluent water samples. In this work, carbon nanofiber coated filter paper used as the sorbent material. In the current separation sciences, carbon based nanomaterials [27-30] such as carbon nanofibers (CNFs) or nanotubes (CNTs) are widely evolving as stationary phases and sorptive materials owing to their rare mechanical and physico-chemical properties and high active surface area. Since the adsorption capacities of CNTs or CNFs are good, it can cause the distortion of planar graphene sheets into a helical or cylindrical structure. In the current approach, the carbon nanofiber was dispersed in polymer, dispersed carbon nanofiber was used to coat the filter paper. A trace amount of 1-octanol was wrapped over the surface and also adhere on the pores of carbon nanofiber coated filter paper that act as a background medium.

The proposed method permits a superior sample agitation and enhances extraction efficacy. Morphological views of carbon nanofiber coated filter paper were captured using scanning electron microscope (SEM). The factors effecting the extraction recoveries including the length of filter paper, pH, extraction time, elution solvent, desorption time, volume of the solvent and effect of adding the salt were optimized.

EXPERIMENTAL

Analytical standards butylparaben (BP, 99.7%), propylparaben (PP, 99.7%), ethylparaben (EP, 99.7%) and methylparaben (MP, 99.7%) were procured from Sigma-Aldrich, India. The individual stock solutions of each parabens were prepared in methanol at 1000 μg mL^{-1} and preserved at 20 ºC. Mixed parabens standard solutions for 10 μg mL^{-1} was prepared by diluting the four parabens stock solutions in methanol. The LC-MS grade acetonitrile, ethyl acetate, isopropanol, acetone and 1-octanol (HPLC grade) was acquired from (Merck Pvt. Ltd. India). Methanol was attained Aencore chemicals from (Rankem, Pvt. Ltd. India). Hydrochloric acid , sodium chloride, sodium hydroxide and nitric acid and sulfuric acid acquired from (S.D. Fine Chemicals, India). Ultrapure water was obtained in the laboratory from ELGA Milli-Q Water System purchased from England. Scharlab (Barcelona, Spain). Carbon nanofiber procured PTFE membrane syringe filter (25 mm, PTFE 0.22 μm) was acquired from Sigma-Aldrich Chemical Pvt Ltd., India. Cellulose filtered paper (4A, 70 mm) was obtained from Merck Pvt. Ltd., India.

Dispersion of carbon nanofiber: The principle factor which influence the surface and mechanical properties is the dispersion of nanoparticles. Carbon nanofibers has a strong tendency to accumulate in the presence of attractive forces like van der Waals, their interaction and the presence of matrices, agglomerates infiltration is hard and also serves as the main source of potential imperfections in nanocomposites. Dispersion can occur either under higher stress (rupture) or lower stress (erosion). When high stress is applied splitting up of agglomerates into small fragments occur whereas under lower stress the constant detachment of small fragments occurs.

In this study, dispersion of carbon nanofibers were tested with different solvents such as DMF, NMP, IPA and acetone. Among the used solvents IPA with poly(ethyleneimine) surfactant showed good dispersion. In the typical process, 100 mg CNFs was added into a 50 mL vial filled with 20 mL isopropanol, later to this mixture 100 mg poly(ethyleneimine) as surfactant was mixed. Then, the vial was vortexed for 2 min and in high power bath, it is ultra-sonicated for 3 h at room temperature. Once the sonication is completed, the solution mixture was used for coating purpose.

Fabrication of CNF coated filter paper: CNF coated filter papers were prepared by a dip-coating method. The bare filter paper was cut with dimensions of 1 cm width and 2 cm length. The filter paper which was cut later immersed into the well-dispersed CNF suspension for 15 s using a clean tweezers and then dried at 50 ºC. For the better layering of CNF on the filter paper, the process was repeated for 10 cycles. Before each dipping, the well-dispersed CNF suspension was stirred using magnetic stirrer for 2 min prior to paper coating process. Once the dipping process is done, the CNF coated papers were stored in clean container for the further work.

Sample preparation and extraction: The waste effluent waters and raw samples (collected from Krishna basin of Guntur, India) (50 mL) were centrifuged at 5400 ×g for 15 min and the supernatant was filtered through a glass fiber filter (37 mm, pore size 1 μm; GE Osmonics, Inc., USA) to separate suspended particulate matter (SPM) from the aqueous fraction. A known concentration of a mixture of labeled internal solutions (IS) (20 to 50 ng/mL) was spiked and allowed to equilibrate for 40 min at room temperature. The SPM was transferred into a preweighed polypropylene tube and spiked with the labeled IS mixture. The samples were equilibrated at room temperature prior to analysis.

Instrumentation: The investigations of parabens matrices were executed using a Shimadzu UPLC-PDA system equipped with an ultra-high pressure quaternary pump (LC-2040C 3D), autosampler and Photodiode Array Detector (Shimadzu, Japan). Data evaluation was accomplished using Lab solutions software version 5.89 (Shimadzu Japan). The good separation of parabens was attained by spursil C_{18} column (250 mm × 4.6mm, 5 µm) with oven temperature at 40 ºC. Acetonitrile and Millipore water were used as a buffer under isocratic elution (75/25%). 0.5 mL min^{-1} was the buffer flow rate, injection volume was 10 µL and 20 min was the total analysis time. The wavelength monitored was 256 nm for all four parabens. The use of spursil C_{18} column provided rapid analysis time and great adept chromatographic separation for four parabens. The morphology of the CNF coated filter paper was captured under the scanning electron microscope using Hitachi, Japan.

Extraction procedure: The systematic extraction procedure of CNF coated filter paper based solid phase extraction. In a typical process, already prepared CNF coated filter paper was taken and soaked in 0.5 mL of 1-octanol for 30 min prior to sample preparation. 10 mL water sample was taken in 15 mL glass bottle, 2 % NaCl is added, subsequently, CNF coated filter paper was dipped in the glass bottle containing the sample solution with the help of crocodile clip. The solution containing filter paper was stirred for 15 min at 300 rpm, during this stage the target parabens are transferred from the sample solution to the extractor phase. After adsorption, the CNF coated filter paper was then picked out and wiped with soft tissue to remove the water. Further, the paper was transferred into the glass tube containing 5 mL of methanol. Then it was shaken by manually for 2 min for the desorption of analytes from the filter paper. When the filter paper was removed, the resulting solution was filtered using a 0.22 µm syringe filter. It is then shifted to a new glass tube and dried using N_2 gas. The final residue was reconstituted by using 100 µL of methanol. The final obtained solution was transferred into a vial and injected into UPLC for the analysis.

RESULTS AND DISCUSSION

Morphology of carbon nanofibre coated filter paper: The morphological views of the CNF coated filter paper have been captured using a field emission scanning electron microscope at an accel-erating voltage of 15 KV. The captured image depicted in Fig. 1a-b shows the bare filter paper under different magnifications. Further, the image captured as well the CNF coated filter paper and the average of the different magnified image for single carbon fiber size is about 100 nm as shown in Fig. 1c-d). This material is responsible for achieving excellent

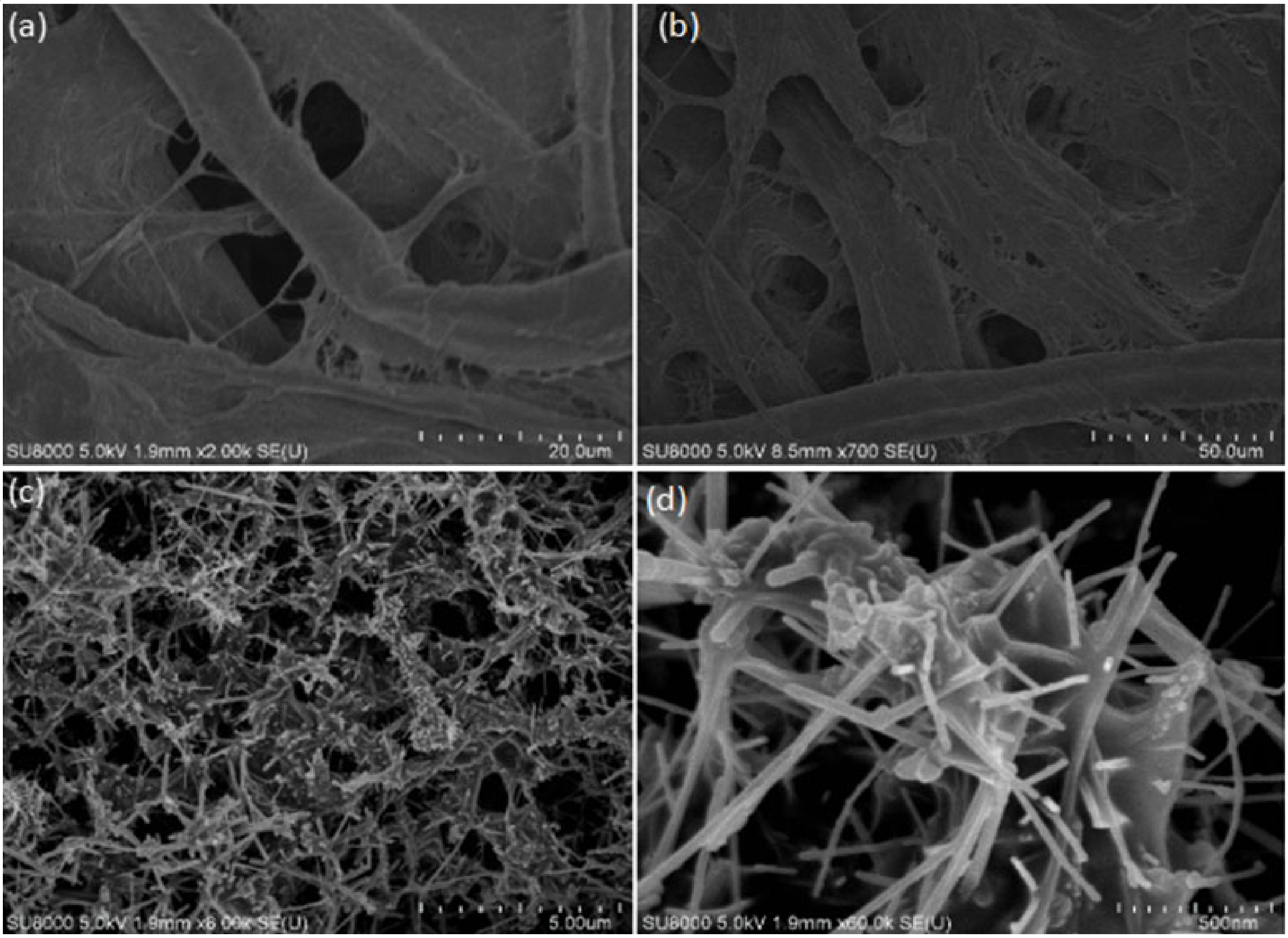

Fig. 1. SEM image of carbon nanofiber coated filter paper

extraction effici-ency by using paper based-SPE technique because of its high sorptive properties and very large surface area.

Optimization of various factors affecting the extraction efficiencies: To get maximum extraction efficiencies using proposed paper based SPE extraction method for detecting parabens from the water samples, the core parameters needed to be optimized are the length of CNF coated paper, sample volume, adsorption time, sample pH, elution solvent, elution solvent volume, desorption time and salt addition. All tests were performed three times parallel to ensure the reproducibility.

Optimization of paper length: The length of CNF coated filter paper is a significant factor in the paper based SPE to get higher extraction recoveries of parabens. In general, the higher quantity of adsorbent favours increases the adsorption efficiency. On another hand, the extra adsorbents may be wasted if a high amount is added than the appropriate. Hence, in present work, various sizes of CNF coated filter paper as an adsorbent (1 × 1, 1 × 1.5, 1 × 2, 1 × 2.5 and 1 × 3 cm) were examined. From the results obtained, the parabens extraction recoveries were increased with increase in the size of paper from 1 × 1 to 1 × 2 cm was noted which is depicted in Fig. 2. This is because of the increase in the length of CNF coated filter paper grad-ually increases the active surface area, π-π interaction of benzene rings in the paraben molecules and also the carbon fiber surfaces. Further to optimize the length of paper, the length of paper was increased from 1 × 2 to 1 × 3 cm and found that there is no notable rise in the extraction recoveries of parabens because the parabens were fully saturated at 1 × 2 cm on the surfaces of CNF coated filter paper. However, from the obtained results it is obvious that 1 × 2 cm of paper length showed higher extraction recoveries of parabens. Thus, 1 × 2 cm of paper length was opted as the optimum length for other studies.

Adsorption (stirring) time: In the adsorption dependent extraction process, suitable adsorption time is an important aspect for the completion of extraction to ease the process of parabens distribution in the paper based SPE extraction process. Here, the adsorption time was performed *via* the simple stirring method. The effect adsorption time on extraction recoveries of extraction of parabens from different water samples was studied in the series of adsorption time at 5, 10, 15, 20 and 25 min, respectively. The extraction recoveries of parabens were extraordinarily enhanced with the raise in adsorption time from 5-15 min. This is due to the sample solution's agitation can fasten the active mass transfer of the analytes amid the sample and adsorbent material resulted in the improvement of the parabens extraction recoveries. Also, there is no notable increase in peak areas of parabens was found and beyond which it is after 15 min as shown in Fig. 3. The reason is the allocation equilibrium between the parabens in water and CNF coated filter paper was already well-established at 15 min as a result no increase in extraction recoveries of parabens. Therefore, 15 min is finalized as optimal adsorption time for further investigations.

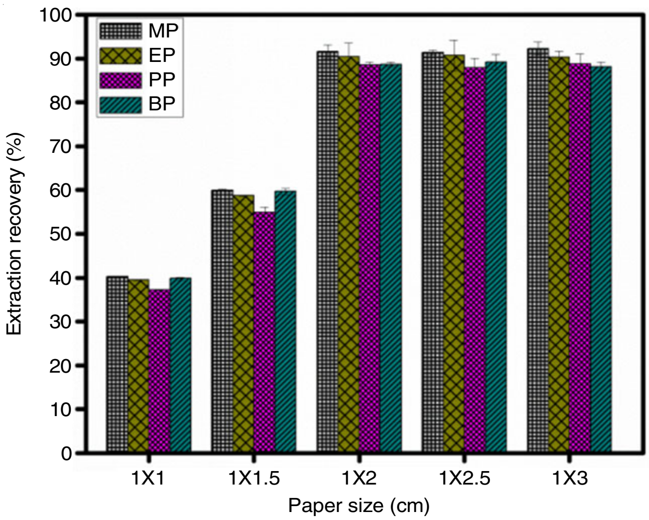

Fig. 2. Optimization of length of carbon nanofiber coated filter paper (n = 3) on extraction efficiencies for the extraction of parabens in water by paper based SPE. Conditions: 10 mL of distilled water spiked with 50 ng mL^{-1} of parabens, pH = 7, adsorption time 15 min, elution solvent methanol, elution solvent volume 5.0 mL, desorption time 2.0 min, addition 2 % of NaCl and stirring rate 300 rpm

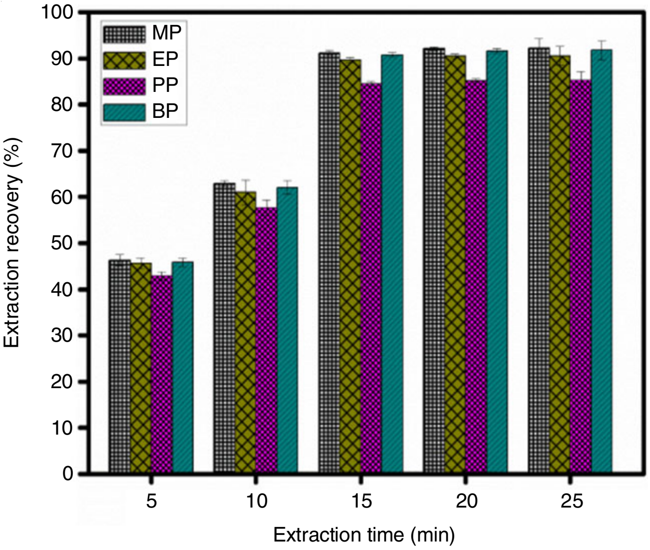

Fig. 3. Effect of adsorption (stirring) time (n = 3) on extraction efficiencies for the extraction of parabens in water by paper based SPE. Conditions: Same as in Fig. 10 except adsorption time (5, 10, 15, 20, 25 and 30 min)

Elution solvent and solvent volume: A suitable elution solvent is a highly considerable analytical factor in the paper-based SPE procedure because the elution solvent is directly associated with the desorption of desired analytes from the adsorbents. Considering the paraben's polarity and solubility, the current work flow, five different organic solvents, namely methanol, acetonitrile, isopropanol, ethyl acetate and acetone were used for the paraben's elution from the sorbent. The acquired results exhibited that acetone showed the very low recoveries of parabens, it might be because of the weaker dispensability of the adsorbent in acetone, it leads to the prevention of the effective desorption of target parabens from the adsorbent. Moreover, methanol, ethyl acetate, acetonitrile and isopropanol own various polarities, this resulted in the reduction of mass transfer from the sorbent. Amongst the solvents used, methanol exhibited highest recoveries of parabens because methanol is more polar compared to other solvent systems, methanol effectively removes all the analytes from the sorbent comparatively with all other solvents as shown in Fig. 4. It is due to the strong interactions with the adsorbent material and this agitate the interaction of parabens with the adsorbent material as a result methanol desorbed the parabens effectively from the adsorbent. Consequently, methanol was utilized as an elution solvent for further investigations.

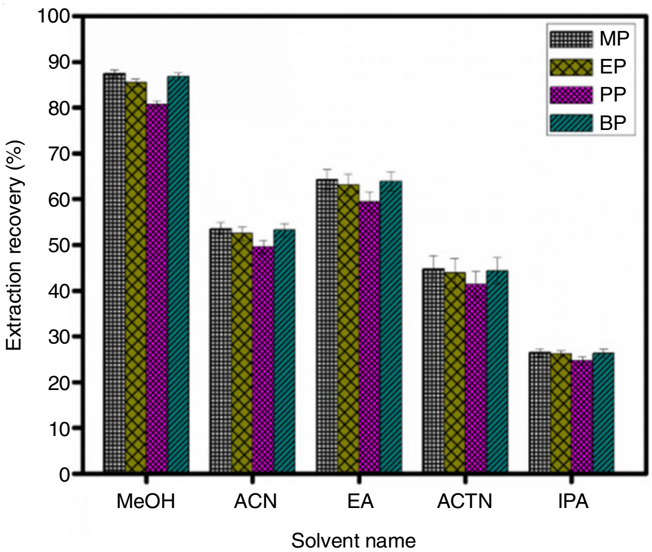

Fig. 4. Screening of elution solvent (n=3) on extraction efficiencies for the extraction of parabens in water by paper based SPE. Conditions: Same as in Fig. 10 except elution solvent (methanol, acetonitrile, ethyl acetate, acetone and isopropanol)

The volume of elution solvent is a significant aspect and must be sufficient for the complete desorption of the parabens from the adsorbent material. Herein, the effect because of the elution solvent volume on the extraction recoveries were carried out by varying the eluent volume as 2, 3, 4, 5 and 6 mL (methanol as ensured from the above analysis). The parabens extraction recoveries were raised slightly as the volume of methanol increased from 2 to 5 mL and the extraction recoveries of parabens attained maximum level when 5 mL was used as depicted in Fig. 5. It indicates that 5 mL of eluent volume is sufficient for the complete desorption of the parabens from the adsorbent. And it also indicates that even by increasing the eluent volume from 5 to 6 mL, the extraction recoveries of parabens were same. The reason is parabens was already reached maximum desorption at 5 mL and not showed the dilution effect due to the final extracted solution was dried and reconstituted in 100 µL of the methanol. The use of more elution solvent volume is time-consuming for reconstitution and effects the environment. Finally, based on the analytical results, 5 mL of methanol was chosen as the best elution volume for further experiments.

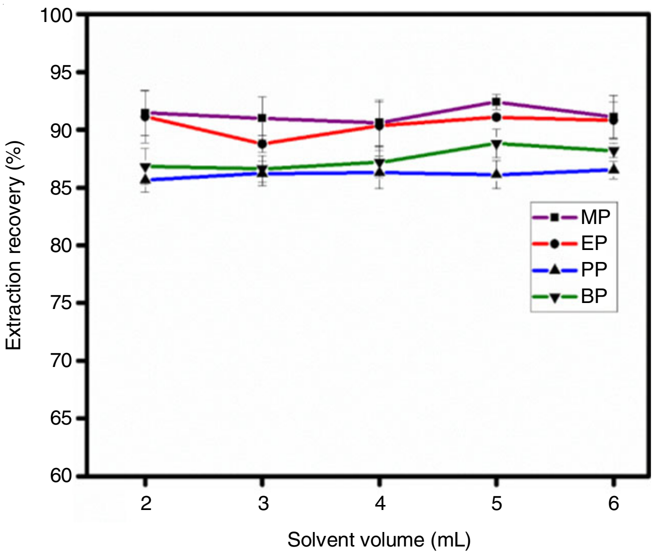

Fig. 5. Effect of elution solvent volume (n = 3) on extraction efficiencies for the extraction of parabens in water by paper based SPE. Conditions: Same as in Fig. 10 except desorption solvent volume (2, 3, 4, 5 and 6 mL)

Desorption time: The required time to desorb the analytes from CNF coated filter paper is called the desorption time. Simple hand shaking was utilized for desorption process as it helps to increase the desorption efficacy. Here, the consequence of desorption time on parabens extraction efficiencies from water samples was studied by changing the desorption time over the range of 1 to 5 min. The parabens extraction recoveries were ultimately increased from 1-2 min rapidly and then maximum desorption was reached at 2 min as shown in Fig. 6. Thereafter the desorption time was raised up to 5 min but there was no potential change in parabens extraction recoveries. The results revealed that the parabens adsorbed were totally desorbed from the carbon cloth within a short time (2 min). This is due to strong interaction between the adsorbent and eluent. Thus, 2 min of desorption time was selected for further investigation.

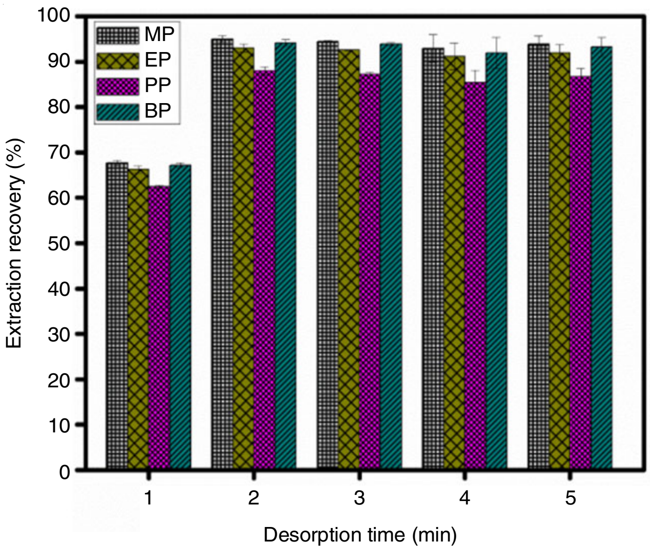

Fig. 6. Effect of desorption time (n=3) on extraction efficiencies for the extraction of parabens in water by paper based SPE. Conditions: Same as in Fig. 10 except desorption time (1, 2, 3, 4 and 5 min)

Stirring rate: The stirring rate is another important effect for the extraction efficiency as it could help to promotes mass transfer of analytes from donor phase towards acceptor phase when the solution was under stirring using a magnetic stirrer. The influence of stirring rate on the parabens extraction recoveries from water was inspected by changing the stirring rate from 100-500 rpm. An increase in the stirring rate of the sample solution from 100-300 rpm results (Fig. 7) in the increase of the analytes mass transfer from donor phase towards the acceptor phase and as a result the parabens extraction recoveries were increased. The continuous increase of stirring rate from 300-500 resulted with no significant effect in parabens recoveries. Based on the acquired results, the highest extraction recoveries were achieved at 300 rpm was established as the optimal for the sample stirring rate.

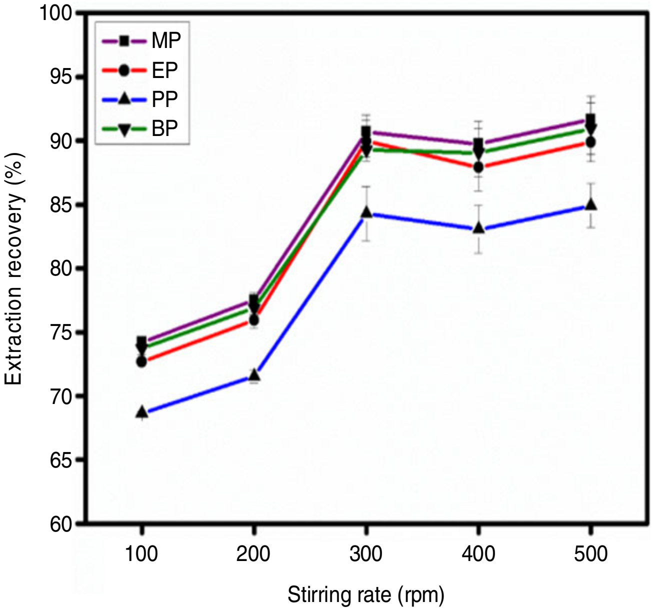

Fig. 7. Effect of stirring rate (n=3) on extraction efficiencies for the extraction of parabens in water by paper based SPE. Conditions: Same as in Fig. 10 stirring rate (100, 200, 300, 400 and 500)

Sample pH: The sample pH is also another significant aspect in typical paper based SPE process. The pH of the sample solution could affect the chemical and even the physical assets of the adsorbent and the adsorbate. The pK_a values of parabens are approximately as for methyl paraben pK_a 8.31 ± 0.13, ethylparaben pK_a 8.31 ± 0.13, butylparaben pK_a 8.22 ± 0.15 and propylparaben pK_a 8.23 ± 0.15, respectively. In proposed work, an influence of sample pH on the extraction recoveries was studied by varying the sample solution pH over the extent of 3 to 9 pH. The parabens extraction recoveries were low at lower pH 3, this is due to the protonation of the oxygen atom present in the ester group (C=O) of parabens. After the parabens extraction, the recoveries were found slowly improved with increase in sample pH from 3 to 7 as showed in Fig. 8. At pH 7, the parabens showed higher parabens extraction recoveries, the reason is that the target analytes binds easily to the material surface at pH 7 *via* hydrophobic and π-π interactions. Further increase in sample pH value 7-9 shows declination in the parabens extraction recoveries it is due to the dissociation of phenolic hydroxyl groups on the parabens occurred slowly. As a result, the hydrophobic interactions between the adsorbent and parabens is decreased which is reflected in the drop of parabens extraction recoveries. Therefore, from the obtained results pH 7 was designated as an optimum pH for further studies.

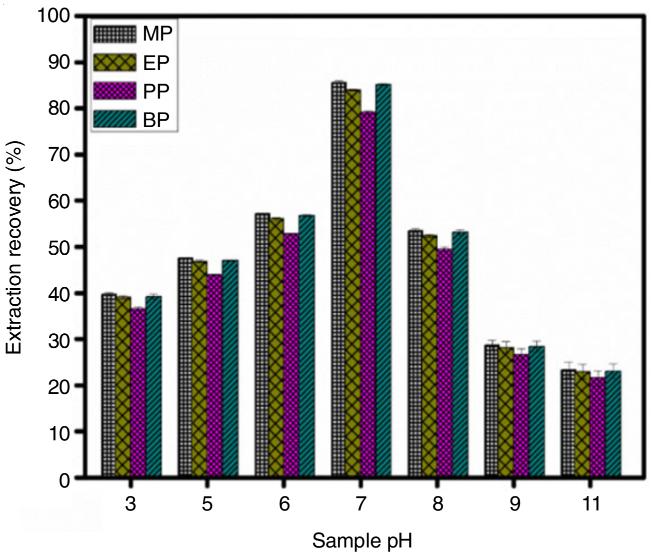

Fig. 8. Effect of sample pH (n=3) on extraction efficiencies for the extraction of parabens in water by paper based SPE. Conditions: Same as in Fig. 10 except sample pH (3, 5, 6, 7, 8, 9 and 11)

Ionic strength: If a salt (electrolyte) is added to the sample solution, it could reduce the solubility factor of the target samples in the aqueous layer and consequently enrich the binding affinity between the sorbent and the analytes (reference). On the other side, the viscosity of the sample solution can also be enhanced leading to the reduction of analyte extraction recoveries. Herein, the salt amount effect was examined by adding different concentrations of sodium chloride (1, 2, 3, 4 and 5%, w/v) and the obtained result is shown in Fig. 9. The parabens extraction efficiencies were increased gradually with the increase in the salt amount from 1 to 2%. This is due to the salt accumulation in the sample solution enhancing the extraction recoveries and by declining the solubility of parabens in the aqueous phase, it enlarges their distribution to the adsorbent from the aqueous solution. Further increasing the NaCl amount from 2 to 5 %,

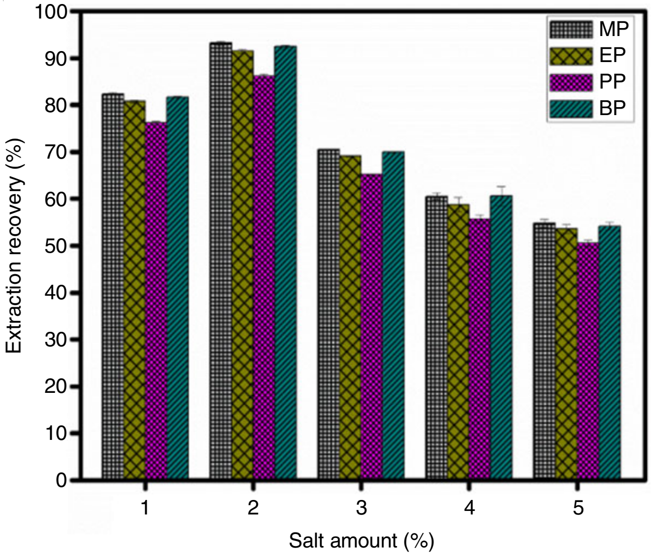

Fig. 9. Effect of salt addition (n=3) on extraction efficiencies for the extraction of parabens in water by paper based SPE. Conditions: Same as in Fig. 10 except salt addition (1, 2, 3, 4 and 5 %)

the parabens extraction recoveries were reduced. The increase in viscosity of the aqueous phase is after the addition of NaCl concentration is increased and decrease in the mass transfer of target analytes to the adsorbent. Therefore, based on the obtained results 2% addition of NaCl to the sample solution was opted.

Analytical applications: To evaluate the proposed method for determination of the four parabens in industrial effluent water samples under the optimum extraction conditions and UPLC conditions, the analytical characteristics such as the linearity, detection limits (LOD), quantification limit (LOQ), precision and recovery were evaluated. As displayed in Table-1, the linearity of the method was examined within concentration range of 0.1-50 ng mL^{-1}. The regression coefficients (R^2) values obtained over the range of 0.9981- 0.9989. Also, the sensitivity of the method was evaluated by calculating the LOQ and LOD based on basis of signal-to-noise ratio. The limits of detection and quantitation were calculated on the basis of signal-to-noise ratio. A signal-to-noise ratio equal to three was employed for limits of detection and a signal-to-noise ratio equal to ten was used for limits of quantitation. The LOQs values found in between the range of 0.75 ng mL^{-1} for both methylparaben and butylparaben, 0.5 ng mL^{-1} for ethylparaben and propylparaben correspondingly. The LODs was found in the range between of 0.1 ng mL^{-1} for ethylparaben and propylparaben, 0.25 ng mL^{-1} for methylparaben and butylparaben representing the proposed method shows extreme sensitive performance. The precision of method was investigated by spiking the parabens standard solution in water at 50 ng mL^{-1} (n=6). The relative standard deviations (RSDs) were found in the range between 0.19-5.72%. The acquired results demonstrated superior linearity, great precision, greater LOQ and LOD ranges proved that the developed method was extremely sensitive in the detection of parabens from effluent water samples.

The current validated proposed method was applied to determine the parabens in four real water samples for instance the swimming pool water, river water, lake and drinking water from local area samples. The obtained analytical outcomes of the 4 different water samples are displayed in Table-2, the results indicated that the parabens were not detected in the real swimming pool water, river water, lake and drinking water samples these results illustrated that the parabens in water samples were lower than the detection limit. The accuracy of method was examined by spiking the water samples at three different concentrations from the low to high level as 0.75, 10 and 50 ng mL^{-1} in the four water samples and the attained results are shown in Table-2. The acquired recoveries were over the range of 95.30-116.72% with RSD less than 5.72%. The attained recovery results clearly representing that the recoveries are in the acceptable range. The typical UPLC chromatograms of tap water samples before and after spiked at 50 ng mL^{-1} displayed in the Fig. 10. The obtained results ensure that the proposed paper based SPE coupled to UPLC-PDA method was highly sensitive, accurate and reliable towards the determination the parabens from the water sample.

Comparison with other reported methods: To demonstrate the advantages of this proposed method, a comparison

TABLE-1
ANALYTICAL FEATURES OF THE METHOD

Analyte	Linear range (ng mL^{-1})	Linear equation	R^2	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Precision (%)
MP	0.1-100	y = 7231.5576x – 4247.6208	0.9981	0.25	0.75	0.96
EP	0.1-100	y = 7712.9213x – 3692.6801	0.9988	0.10	0.50	0.97
PP	0.1-100	y = 11641.450x – 6979.0062	0.9988	0.10	0.50	0.87
BP	0.1-100	y = 13083.295x – 7659.9042	0.9989	0.25	0.75	0.74

MP = Methyl paraben, EP = Ethyl paraben, PP = Propyl paraben, BP = Butyl paraben

TABLE-2
REAL SAMPLE ANALYSIS AND RECOVERIES

Analyte	Spiked (ng mL^{-1})	Swimming pool water			River water			Lake water			Drinking water		
		Found (ng mL^{-1})	RR (%)	RSD (%)	Found (ng mL^{-1})	RR (%)	RSD (%)	Found (ng mL^{-1})	RR (%)	RSD (%)	Found (ng mL^{-1})	RR (%)	RSD (%)
MP	0	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.75	0.87	116.21	2.04	0.83	111.72	2.60	0.85	116.72	0.73	0.84	112.78	0.43
	10	9.79	97.93	0.50	9.61	96.14	1.58	10.57	99.78	3.12	9.9	99.03	3.22
	50	52.33	105.04	1.83	53.82	108.21	0.37	54.96	113.76	4.90	57.46	117.16	1.74
EP	0	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.75	0.79	105.73	2.16	0.82	109.36	0.52	0.79	106.24	1.94	0.80	107.46	0.56
	10	9.68	96.83	0.93	9.56	95.61	0.47	10.54	99.22	0.03	9.98	98.45	0.62
	50	52.38	105.00	2.03	51.70	103.17	0.59	57.90	107.51	1.45	55.92	112.72	0.63
PP	0	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.75	0.87	115.29	1.33	0.84	111.92	0.55	0.85	112.67	0.70	00.86	115.12	0.65
	10	9.65	96.54	0.55	9.53	95.30	1.53	10.61	100.66	5.72	9.82	98.29	2.90
	50	51.83	103.97	1.71	53.12	106.89	0.33	52.63	112.68	4.51	56.48	114.13	0.07
BP	0	ND	–	–	ND	–	–	ND	–	–	ND	–	–
	0.75	0.86	115.89	0.56	0.86	114.72	1.57	0.85	111.24	0.17	0.85	113.88	1.40
	10	9.71	97.15	0.19	9.57	95.68	1.62	10.89	99.21	2.65	9.77	97.76	2.56
	50	51.10	102.32	1.17	50.51	101.48	0.73	55.92	105.68	0.21	54.21	108.60	0.23

TABLE-3
COMPARISON OF PROPOSED METHOD WITH OTHER REPORTED LITERATURE

Analyte	Extraction method	Instrument used	Extraction time (min)	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Recovery (%)	Precision RSD (%)	Ref.
MP, EP, PP, BPB, iPP, iBP, PP, PHP	DMSPE	GC-MS	20	0.03-2	0.1-6.7	81-119	5.3-9.2	[8]
MP, EP, PP and BP	MSPE	HPLC-DAD	20	0.02-0.09	0.05-0.28	80.3-117.3	1.1-14.9	[31]
MP, EP, PP and BP	MSPE	LC-MS/MS	21	0.26-1.35	0.87-4.50	88-97	4.2-8.3	[32]
MP, EP, PP and BP	Multi-stir-rod	HPLC-DAD	25	0.63-0.80	2.12-2.67	83-103	1.11-7.79	[33]
MP, EP, PP and BP	SPE	HPLC-DAD	45	0.5-2.1	2-5.3	82-104	4.3-7.6	[34]
MP, EP, PP, BP and BZP	VA-SPE	LC-MS/MS	20	0.09-0.45	0.36-1.8	78.75-102.1	0.9-7.4	[35]
MP, EP, BZP and TCC	BAμE	HPLC-DAD	120	0.2-6.5	0.64-20	65-123	3-22	[36]
MP, EP, PP and BP	Paper based SPE	UHPLC-PDA	15	0.1-0.25	0.5-0.75	95.30-116.7	0.74-0.97	Proposed method

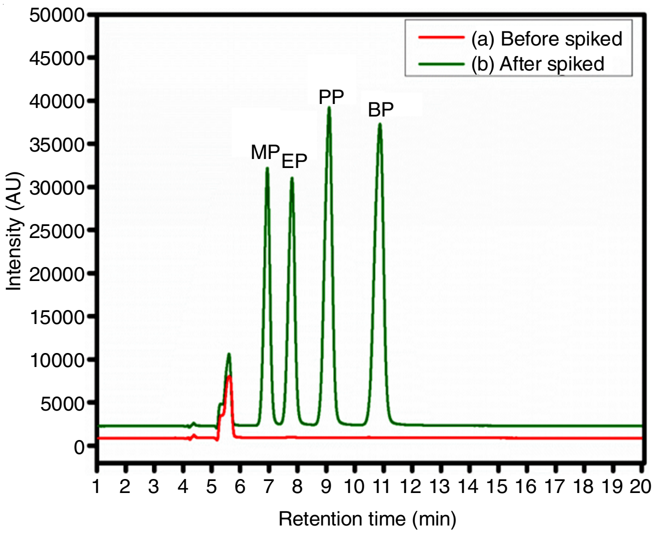

Fig. 10. UPLC chromatograms of tap water sample (a) before spiked and (b) after spiked (50 ng mL^{-1}) by this extraction procedure

between the developed paper based SPE coupled with UPLC-PDA method and others reported methods [8,31-36] and micro-extraction methods [37-39]. Published literature compared with current proposed method is displayed in Table-3. From the outcomes, we can assure that the proposed method represents short extraction time and the repeatability values are low when compared to the majorities of all other approaches. Then again, this developed method presents similar detection limit, quantification limit and recoveries. These results demonstrate that the developed method was easy, fast, highly sensitive towards the target analyte and low cost compared to all the other reported analytical techniques.

Conclusion

A novel SPE-UPLC-PDA method for the concurrent analysis of methylparaben, ethylparaben, propylparaben, butyl paraben in water samples has been reported. A novel validated SPE-UPLC-PDA technique is an easy, rapid, environmental-friendly and also decreases the organic solvents consumption to meet the demand for principles of green analytical chemistry and its applications to the real sample analysis. The current proposed technique allows greater sample agitation and mainly improves extraction recovery. This proposed method offers tremendous linearity, lower organic solvent usage, good accuracy, repeatability and short extraction time, Superior sensitivity was achieved by carbon nanofiber coated paper because of its high sorptive properties, superior porosity and large surface area claim its practical applications in near future.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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