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Preconcentration of heavy metals on multiwalled carbon nanotubes in water samples prior to analysis using FAAS

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ABSTRACT

In the present work, multiwalled carbon nanotubes (MWCNTs) a solid phase extraction sorbent has been described for the preconcentration of trace amounts of some heavy metals in water samples prior to their determination by flame atomic absorption spectrometry. The effect of different parameters has been thoroughly studied and applied the optimum experimental conditions. The calibration was performed using aqueous standard solutions with an enrichment factor of the preconcentration was 10. The calibration graphs were linear with the correlation coefficient range 0.9994–0.9999 under the optimized conditions. The developed method was then applied for the determination of copper, cadmium, chromium, zinc and iron in water samples by flame atomic absorption spectrometry (FAAS). The detection limits under these conditions were 5.46, 2.97, 5.0, 0.96, and 7.94 μg L^{-1} for Cu, Cd, Cr, Zn and Fe, respectively. The relative standard deviations (RSDs) for five replicate samples were found to be less than 3.0%. The percentage recoveries of metals in spiked samples were found to be in the range of 90.5%–99.0%. The standard reference materials (NIST SRM 3108, 3112a, 3114, 3126a, and 3168a) were used to verify accuracy of this method. This procedure was successfully applied to the determination of these metals in water samples with satisfactory results and recommended to apply in all desalination plants samples.

Keywords: Multiwalled carbon nanotubes; Heavy metals; FAAS; Preconcentration; Solid phase extraction

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1. Introduction

The determination of heavy metals in water at low levels is an important issue for water quality and research area. Because of that, the development of sensitive and selective techniques are in great demand to obtain the detection limits. Heavy metals are toxic and harmful even at low level exposure, not only to the human beings but also to the aquatic animals and plants due to their toxicity and non-biodegradability [1,2]. Therefore, it is an important to determine the concentration of these elements in water samples accurately. Use of flame atomic absorption spectrometry (FAAS) technique is very attractive for routine metal determinations [3,4]. Due to low level of trace elements in real samples, the sensitivity of AAS is very low. To overcome the low sensitivity of FAAS, a preconcentration step prior to the instrumental analysis is mandatory [5–8].

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Among of various preconcentration procedures, solid phase extraction (SPE) is the most suitable procedure to heavy metals determination [9–11]. Therefore, developing and applying new quantitative detection methods based on SPE is reasonable and promising for accurate and rapid measurement of metals in low levels. It showed high repeatability and selectivity, was economic and could be used with samples of large volume [12,13]. Multiwalled carbon nanotubes (MWCNTs) have shown superior properties as SPE sorbent for the preconcentration of heavy metals. They have a high tensile strength and stability in acid and basic medium, as well as the ability to interact with various organic and inorganic analytes [14–20].

Krawczyk and Jeszka-Skowron used MWCNTs as solid sorbent for the sequential determination of cadmium and lead in water samples and they reported the concentration limits of detection were 0.001 and 0.03 μg L^{-1} for Cd and Pb, respectively [21]. Tuzen and Soylak adsorbed chromium(III) and chromium(VI) using MWCNTs and they reported a detection limit of 0.90 mg.L^{-1} [22]. Zhou et al. established a SPE method to determine nickel (Ni^{2+}), cobalt (Co^{2+}) and mercury (Hg^{2+}) ions using MWNTs and sodium diethyldithiocarbamate (DDTC) as the adsorbent and the chelating agent, respectively, and performed the analysis on a high performance liquid chromatography (HPLC) with a detection limit between 0.04 and 0.90 μg L^{-1} [23]. Stafiej and Pyrzynska evaluated carbon nanotubes (CNTs) for the SPE of some metals including Cu(II), Co(II), Ni(II), Zn(II), Pb(II), Mn(II) and Cd(II) [24]. A new method was investigated by Crecente et al. for the Pb separation using MWCNTs as a SPE sorbent and determination by electrothermal atomic absorption spectrometry (ETAAS). The detection and quantification limits obtained were 0.08 and 0.26 μg L^{-1}, respectively [25]. Chen et al. applied single-walled carbon nanotubes (SWCNTs) for the separation of Cu(II), Co(II) and Pb(II) before using inductively coupled plasma mass spectrometry (ICP-MS) and they reported a detection limit of 39, 1.2 and 5.4 mg.L^{-1} for Cu(II), Co(II) and Pb(II), respectively [26]. Liang et al. developed a new method using a microcolumn packed with MWCNTs as sorbent for the preconcentration of trace amount of Au prior to its determination by FAAS. The detection limit of this method for Au was 0.15 μg L^{-1} [27]. However, the application of MWCNTs in water samples is still provides low detection limits (LODs) and improvement in their adsorption capacity for the analysis of trace elements.

The purpose of the present work was to establish a novel method at shoaiba desalination plant for the determination of heavy metals in water samples. In the procedure, we used the MWCNTs as SPE adsorbent for the preconcentration of trace amounts for some heavy metals in water samples of shoaiba desalination plant. This research work is concerned with the determination of toxic metals in water samples by FAAS after preconcentration of glass column packed with MWCNTs.

2. Experimental

2.1. Material and reagents

All chemicals and reagents used were of analytical reagent grade. Demineralized water of high purity (Milli-Q Millipore 18.2 MΩ.cm^{-1} conductivity) was used for all dilutions and preparation in our experiments. Stock standard solutions (1,000 µg·mL^{-1}) for Cu, Cd, Cr, Zn and Fe were obtained from BDH (Poole, UK). Nitric acid 69%–71% was purchased from Loba Chemie. Ltd. (Mumbai, India). The following buffer solutions were used to adjust the pH of the solutions: H_3PO_4-$NaH_2PO_2H_2O$ (pH 2), NaH_2PO_4-NaOH (pH 3–8) and were purchased from BDH (Poole, UK). A standard reference materials, (NIST SRM 3108, 3112a, 3114, 3126a, and 3168a), were obtained from National Institute of Standards and Technology (NIST, Kingstown, RI 02852, USA). MWCNTs with purity more than 95% and density 2.1 g/cm^3 at 20°C, was purchased from Chengdu Alpha Nanotechnology Ltd., (Chengdu, China). All the glassware and plastic were cleaned by soaking in dilute HNO_3 2% and were rinsed with distilled water before were use.

2.2. Instruments

A Shimadzu Model 6,800 atomic absorption spectrometer was used for the determination of metals. Studies were carried out in an air/acetylene flame with deuterium background correction. The operating parameters for the metal ions were summarized in the Table 1. A Mettler Toledo pH-S220 Model glass-electrode pH meter was employed to measure pH values in the aqueous phase.

2.3. Column preparation

0.42 g of MWCNTs was loaded into a 10 × 100 mm glass column plugged with a small portion of glass wool at both ends. The resin bed was approximately 2 cm. The column was washed by passing 15 mL of 1 mol.L^{-1} HNO_3 solution and 20 ml of water, respectively. The column was preconditioned by passing a blank solution prior to each use. After elution, the resin in the column was rinsed with a 15–20 mL of the eluting solution and water, subsequently, and stored for the next experiment.

Table 1
The instrumental settings for the flame atomic absorption spectrometer

Parameter	Copper	Cadmium	Chromium	Zinc	Iron
Wavelength, nm	324.8	228.8	357.9	213.9	248.3
Lamp current, mA	6.0	8.0	10	8.0	12
Spectral bandwidth, nm	0.5	1.0	0.5	0.5	0.2
Air flow rate, dm^3 min^{-1}	8.0	8.0	8.0	8.0	8.0
Acetylene flow rate, dm^3 min^{-1}	1.8	1.8	2.8	2.0	2.2

2.4. Sample collection and preparation

All samples were collected from different places in all shoaiba desalination plant and halli dam. These samples including seawater, product water and dam water samples. Because of sea water samples contain a large amounts of salts, we recommended to dilute all sea water samples prior to apply the preconcentration method for the determination of metals. For the dilution of seawater sample, 75 mL of seawater sample was diluted to 200 mL with demineralized water. and then acidified to 2% v/v HNO_3 and heating was started at 60°C for 2 h digestion of seawater sample. All samples were filtered through Whatman paper No.1 a 0.45 µm membrane filters to remove any fine particulate matter present. The pH of the samples was adjusted to the desired pH with buffer solution, and the preconcentration procedure was then applied to these samples. The retained metals on MWCNTs were eluted with 15 ml of 1 M HNO_3 solution and then 15 mL of demineralized water at a flow rate of 4 mL.min^{-1}, respectively. The metal concentrations in the eluent were determined by flame AAS.

2.5. Preparations of standard solution

A standard solution (0.1 mg.L^{-1}) were prepared from 1,000 mg.L^{-1} stock standard solutions of Cu, Cd, Cr, Zn and Fe for FAAS.

2.6. Preconcentration procedure

The present method was first tested with model solutions. A 100 ml of solution containing 10 µg of Cu, Cd, Cr, Zn and Fe was brought to the desired pH (between 2 and 8). The column was preconditioned with 15–20 ml of the water adjusted to the same pH as that of the working solution. Then, the mixture was allowed to pass through the glass column packed with MWCNTs at a flow rate of 4 ml.min^{-1}. The retained metals on MWCNTs were eluted with 15 ml of 1 M HNO_3 solution and then 15 mL of demineralized water at a flow rate of 4 mL.min^{-1}, respectively. Then, the column was washed with the same buffer solution as that used for preconditioning. Afterward, the concentrations of the analytes in the eluent were analyzed by flame AAS.

3. Results and discussion

3.1. Effect of pH

To study the best parameters for the extraction of metal ions, it is well known that the pH of an aqueous sample is one of the most important factor in the extraction efficiency of metal ions in SPE studies [26,28,29]. Therefore, the effect of pH on the adsorption of Cu, Cd, Cr, Zn and Fe onto MWCNTs was investigated over the range from 2 to 8 using standard solutions containing 0.1 mg.L^{-1} for each element while keeping other experimental parameters constant and adjusting with buffer solutions in order to obtain the optimal pH for the adsorption of each analyte ion. The extraction efficiencies were calculated on the basis of the difference concentration between the spiking and actual one measured. We have observed that, the extraction efficiency is dependent upon the pH of the solution. The results indicated that extraction efficiency values decreased beyond pH 8.0, due to the fact that an increase of pH higher than 8.0 lead to the precipitation of the heavy metals. The surface isoelectric point of MWCNTs shifts to lower pH values upon neutralization of the MWCNTs' surfaces, so cation adsorption decreases quickly [30]. The effect of various pH values on the extraction efficiency is shown in Fig. 1. It can be seen that the optimum pH for extraction efficiency (>99%) of metal ions was observed at pH 8.0. Therefore, all subsequent experiments was performed at pH 8.0.

3.2. Effect of sample flow rate

The sample flow rate through the column that has been filled with MWCNTs is a very important parameter, since this is one of the most steps that control the analysis time. The influence of the sample flow rate on the preconcentration efficiency of Cu, Cd, Cr, Zn and Fe on MWCNTs was tested at flow rates of 2.0 and 4.0 mL min^{-1}. In a comparison between both flow rates 2.0 and 4.0 mL min^{-1}, we observed that no significant effect on the recoveries of the investigated elements. These results are given the best indication and advantage for the analysis of samples in short time. Therefore, a sample flow rate of 4.0 mL min^{-1} was selected for further studies (Fig. 2).

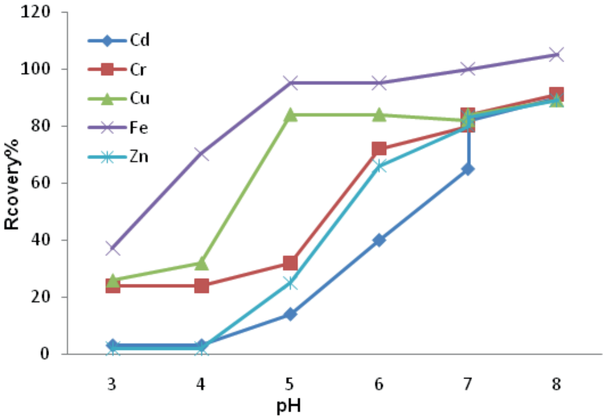

Fig. 1. Effect of pH on extraction of Cu, Cd, Cr, Zn and Fe onto MWCNTs.

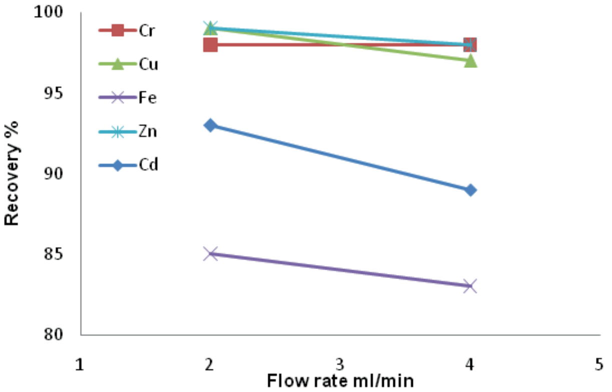

Fig. 2. Effect of flow rate on the recovery of Cu, Cd, Cr, Zn and Fe.

3.3. The optimization of elution conditions

3.3.1. Type of eluent

The type of eluent is one of the most important factors to enhance the extraction efficiency. For this study, a hydrochloric and nitric acid were used as eluents for the heavy metal ions elution from MWCNTs column. As it is shown in Table 2, the extraction efficiency using nitric acid as eluent for the analyte ions is the best eluent in experiments. The extraction efficiency values for all analyte ions were higher than 90% with 1.0 mol.L^{-1} HNO_3. Thus, HNO_3 had a better elution performance than HCl due to its oxidative action and stronger dissolution ability.

3.3.2. Concentration of eluent and volume

The effect of eluent concentration and volume on the recoveries of Cu, Cd, Cr, Zn and Fe were investigated. 15 mL of various concentrations (0.01, 0.1, and 1 mol.L^{-1}) of HNO_3 were studied for the desorption of the retained analytes from the column. Fig. 3 shows the effect of various concentrations of eluent on the recovery of 0.1 µg.mL^{-1} of the analytes. It was found that 1.0 mol.L^{-1} HNO_3 was sufficient for quantitative elution (>91%). The effect of the volume of eluent on the extraction efficiency values of the analytes was also investigated with different volumes of 1.0 mol.L^{-1} HNO_3 as eluent. Effect of eluent volume values on the recoveries is shown in Table 3. It was found that the highest extraction efficiency (>94%) could be achieved with 15 mL of 1.0 mol.L^{-1} HNO_3, which sufficient for quantitative elution. Therefore, the eluent volume of 15 mL of 1.0 mol.L^{-1} HNO_3 was used in the following experiments.

Table 2
Effect of eluent type on the recovery of Cu, Cd, Cr, Zn and Fe

Type of eluent	Extraction efficiency %				
	Cu	Cd	Cr	Zn	Fe
HCl 1.0 mol.L^{-1}	103	88	90	98	81
HNO_3 0.01 mol.L^{-1}	68	60	53	58	34
HNO_3 0.1 mol.L^{-1}	75	82	67	85	38
HNO_3 1.0 mol.L^{-1}	102	91	92	99	91

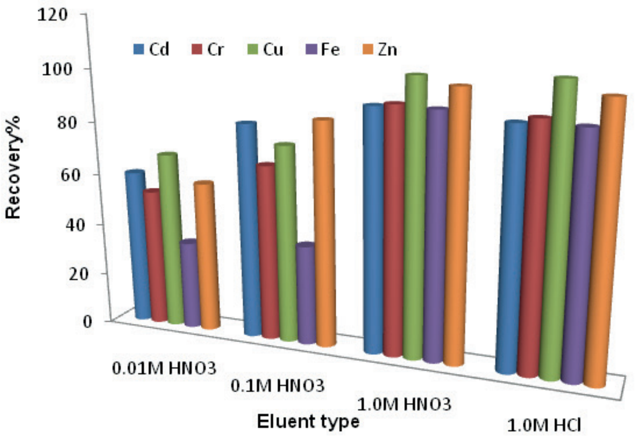

Fig. 3. Effect of the eluent type and concentration on the recovery of Cu, Cd, Cr, Zn and Fe.

3.4. Adsorption capacity

Adsorption capacity of the adsorbent is an important parameter for the evaluation of the adsorption, due to it determines how much sorbent is efficient and quantitative recovery can be obtained the analytes from a given solution. The maximum adsorption capacity of MWCNTs with respect to Cu, Cd, Cr, Zn and Fe ions has been studied by passing 150 mL aliquot of a series of concentrations (0.5–100 mg.L^{-1}) through the column at the appropriate pH, followed by its determination in the effluent and in the eluted solution using FAAS. The maximum capacities of this sorbent were found as 7.7, 7.8, 7.5, 7.0, and 8.1 mg.g^{-1} for Cu, Cd, Cr, Zn and Fe, respectively.

3.5. Column reusability

The long-term stability of MWCNTs was subjected by successive adsorption and desorption cycles of 100 mL sample solutions containing 0.1 mg L^{-1} of analytes at the optimum condition. Afterward, the adsorbed metal ions were eluted with 10 mL of 1 mol.L^{-1} HNO_3 solution. By monitoring the change in the recoveries of the extraction of analytes, the stability of the adsorption was represented to be 55 repeated adsorption–desorption cycles without any significant loss in its adsorption capacity.

3.6. Applications of the presented procedure

The accuracy of the method was tested using the standard reference materials (SRM) (NIST SRM 3108, 3112a,

Table 3
Effect of eluent volume on the recovery of Cu, Cd, Cr, Zn and Fe

Volume of HNO_3 eluent	Extraction efficiency %				
	Cu	Cd	Cr	Zn	Fe
12	79	92	79	85	74
15	96	96	97	97	94
20	78	96	79	84	88

Table 4
Results of the analysis of certified reference material and the certified values

Metal	Standard reference material	Certified value (µg L^{-1}) ± SD[a]	Found value (µg L^{-1}) ± SD
Cu	NIST-3108	5.0 ± 0.03	4.8 ± 1.82
Cd	NIST-3112a	5.0 ± 0.03	4.8 ± 0.99
Cr	NIST-3114	5.0 ± 0.04	4.0 ± 1.66
Zn	NIST-3126a	5.0 ± 0.08	5.1 ± 0.32
Fe	NIST-3168a	5.0 ± 0.18	4.5 ± 2.64

[a] SD, Standard deviation.

3114, 3126a, and 3168a) for Cu, Cd, Cr, Zn and Fe, respectively, simulated fresh water. The results (n = 5 for each analysis) were shown in Table 4, are in good agreement with the certified values. By assuming the certified values are the true values, the *t*-test was applied to the results. The results passed the *t*-test at 95% confidence level. Aqueous standard solutions were used for the calibration plots.

The relative standard deviation of the proposed method in the range 0.76%–3.82% was compared to the relative standard deviation of the certified value for NIST SRM that found to be within ± 2.5%.

3.7. Detection limits and precision

The detection limits (DL) of the presented method for Cu, Cd, Cr, Zn and Fe, were studied under the optimized experimental conditions using blank solution. Based on

Table 5
Analytical characteristics of the calibration curves of the analytes

Analyte	Correlation coefficient	Linear range (mg L^{-1})	DL (μg L^{-1})	RSD %
Cu	0.9999	0.05-2	5.46	2.87
Cd	0.9998	0.05-2	2.97	1.88
Cr	0.9994	0.05-2	5.00	1.63
Zn	0.9999	0.05-2	0.96	2.98
Fe	0.9998	0.05-2	7.94	2.42

Table 6
Determination of analyte elements in water samples

Analyte	Water samples, μg L^{-1}		
	Product water	Dam water	Sea water
Cu	32 ± 0.80	4.6 ± 0.05	5.3 ± 0.10
Cd	3.0 ± 0.02	2 ± 0.10	3.1 ± 0.03
Cr	3.0 ± 0.01	2.4 ± 0.20	3.2 ± 0.05
Zn	0.55 ± 0.00	0.89 ± 0.00	3.85 ± 0.10
Fe	5.4 ± 0.03	8.6 ± 0.50	17.1 ± 0.20

Table 7
Addition/recovery test as the application of the presented method

Analyte	Seawater		
	Added (μg.L^{-1})	Found (μg.L^{-1})	Recovery (%)
Cu	0	5.30	–
	10	14.8	95
Cd	0	3.10	–
	10	13.0	99
Cr	0	3.20	–
	10	12.8	96
Zn	0	3.90	–
	10	12.9	90
Fe	0	17.1	–
	10	26.9	98

Table 8
Comparison of the presented work with other SPE methods for the preconcentration of heavy metals

Adsorbent	Analytes	Instrument	P.F[a]	LOD[b] (μg L^{-1})	RSD[c] (%)	Ref
MWNTs	Cu^{2+},Co^{2+}, Ni^{2+}, Pb^{2+}	FAAS	40	1.64–5.68	NM[d]	[31]
MWNTs /ammonium pyrrolidine	Cu^{2+},Cd^{2+},Pb^{2+},Zn^{2+},Ni^{2+}, Co^{2+}	FAAS	80	0.30–0.60	≤ 5.0	[32]
MWNTs	Co^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Cr^{3+}, Ni^{2+}	FAAS	50	0.24–2.60	1–17	[33]
MWCNTs	Cu^{2+}	FAAS	60	1.46	NM	[34]
(TETA- MWCNT)	Pb^{2+},Cu^{2+}, Ni^{2+} Cd^{2+}	FAAS	113	0.3–3.7	≤4.7	[35]
MWCNT	Pb^{2+}, Zn^{2+}, Ni^{2+} Cd^{2+}	FAAS	15	1.2–7.2	<5.0	[36]
(MWCNTs-cysteine)	Cd^{2+}	FAAS	33	0.28	≤5.0	[37]
SPE	Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}	FAAS	67	2.4–41.4	<4.1	[38]
Bacillus sphaericus-loaded Chromosorb 106 (BSLC106)	Ni^{2+}, Ag^{+}	FAAS	25	1.42, 1.05	NM	[39]
MBMP	Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{+3}, Mn^{+2}, Ni^{2+}, Pb^{2+}, Zn^{2+}	FAAS	20	0.33–0.9	≤4.0	[40]
QAN	Co^{2+}, Cu^{2+}, Fe^{+3}, Pb^{2+}, Mn^{+2}	FAAS	100	0.03–0.83	<3.5	[41]
SPE	Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{+3}, Mn^{+2}, Ni^{2+}, Pb^{2+}, Zn^{2+}	FAAS	100	0.06–0.67	≤ 1.5	[42]
MWCNTs	Cu^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Fe^{2+}	FAAS	10	0.96–7.94	<3.0	This work

[a] PF, Preconcentration factor; [b] LOD, Limit of detection; [c] RSD, Relative standard deviation; [d] NM, Not mentioned.

three times the standard deviation of eight runs of the blank solution, they were found to be 5.46, 2.97, 5.00, 0.96, and 7.94 μg L^{-1}, respectively. The relative standard deviation (RSD) of this method for Cu, Cd, Cr, Zn and Fe were 2.87%, 1.88%, 1.63%, 2.98%, and 2.42%, respectively. The analytical characteristics of the calibration curves of the analytes in the present work is given in Table 5.

3.8. Application of the presented procedure

The presented procedure was applied to the determination of heavy metals in water samples. The results of heavy metal concentrations in water samples are shown in Table 6. The accuracy of the results for the study was confirmed by analyzing spiked seawater sample after the addition of known amounts of the target analytes into 200 mL of seawater sample. A good agreement was obtained between the added and measured analyte amounts in seawater sample and the results are given in Table 7. The recovery of spiked samples was satisfactory, and hence the presented method could be applied successfully for the separation, preconcentration and determination of trace amounts of Cu, Cd, Cr, Zn and Fe ions in real samples.

4. Conclusion

The adsorption of Cu, Cd, Cr, Zn and Fe by using MWCNTs as a SPE sorbent for the preconcentration prior to their determination by FAAS is proven to be easy and precise technique and can be applied to water samples. The adsorption capacity of MWCNTs is high toward metal ions and the retained analytes on MWCNTs can be easily desorbed. The recovered concentrations for certified reference materials were in good agreement with the reference values. The proposed preconcentration method was applied to determination of analyte ions from water samples were collected from Shoaiba desalination plant and halli dam in Saudi Arabia. It can also be conclude that the concentrations of Cu, Cd, Cr, Zn and Fe obtained in water samples were found to be within international acceptable limits. The comparative data between some recent works with other SPE methods and the presented work for the preconcentration of heavy metals ions are shown in Table 8. The proposed work is simple and accurate for the preconcentration and flame atomic absorption spectrometric determination of targeted elements at trace levels. The preconcentration factor are generally better than those obtained by some presented methods given in Table 8. We recommend that to apply this method in laboratories due to it can be easily use for routine analysis of water samples.

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