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Solid-phase extraction of copper and zinc in water samples using diethylamine-modified phosphorus-containing polymer

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ABSTRACT

Diethylamine-modified phosphorus-containing polymer has been used as adsorbent for the preconcentration of traces amounts of Cu(II), and Zn(II). 4-(2-thiazolylazo) resorcinol was used as a chelating agent. The analytes were determined by FAAS. Various parameters such as: pH, volume of ligand, volume of elution, and eluent concentration affecting on the extraction efficiency of the polymer has been evaluated by Placket–Burman design to explore the important variables. Further were optimized by central 2^{3+} star orthogonal composite design. The limits of detection for Cu(II) and Zn(II) were 2.1 and 6.3 μg/L, respectively. The accuracy of proposed method was checked by the analysis of TMDA 64.2 certified reference material. The method was applied to determine Cu and Zn in natural water samples.

Keywords: Solid-phase extraction; Preconcentration; Copper; Zinc; Multivariate study

1. Introduction

Some heavy metals at trace levels are essentials and play very important role in human metabolism. Contrary, at higher concentrations most of the elements are toxic. Therefore, the accumulation of heavy metals in soil, irrigated water, and food stuffs was an important issue in environmental and biological science [1–3]. There are the several adverse impacts on humans from trace elements and as well as animals but few of them are most important such as brain, kidney, nervous system, and reproductive system. The metals may replace the essential nutrients from human body. They are adjoining their sites to the vital organs of human body [4].

The determination of metal ions at trace level by flame atomic absorption spectrometry has a several advantages such as good selectivity, speed, and fairly low-operational cost. Direct determination of trace elements at extremely low concentration was often very difficult due to the insufficient sensitivity of the methods and the matrix interferences [5,6].

Multivariate technique has been widely used in the optimization of procedures in analytical chemistry. Multivariate technique is fast, cost-effective, and allows more than one variable to be optimized simultaneously [7,8]. In this technique, the different groups of designs such as Plackett–Burman designs (PBDs) [9]

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and central composite design (CCD) were used to determine the main variables affecting the extraction efficiency [10].

Several separation and preconcentration methods include cloud point extraction, liquid–liquid microextraction, coprecipitation, flotation, and solid-phase extraction (SPE) have been widely used throughout the world. SPE is one of the most common techniques and which was used for preconcentration of analytes because of factors like high concentration, simple operation, economically cheap, absence of emulsion, and minimum amount of organic solvents were used without any contamination in the laboratory work [11–18]. Therefore, SPE method was named as environmentally friendly technique [19–26].

In the present study, diethylamine-modified phosphorus-containing polymer (DPCP) was prepared from the reaction between phosphorus-containing polymers [27,28], and DPCP was used for the preconcentration and separation of the trace amount of copper and zinc in natural water samples. Four factors influencing the extraction efficiency of understudy metals were investigated by PBD and CCD designs.

2. Experimental

2.1. Chemical and reagents

All the reagents and chemicals of E. Merck (Darmstadt, Germany) were used of analytical grade. Distilled/deionized water (Millipore Milli-Q system 18 MΩ/cm resistivity, Bedford, MA, USA) was used throughout the work. Concentrated nitric acid (65%) of spectroscopic grades (E. Merck, Darmstadt, Germany) was used. Stock standard solutions (1,000 mg/L) of understudy metal ion were prepared by dissolving appropriate amounts of nitrate salts in 1% nitric acid. While working, standards of corresponding metal ions were prepared from the dilution of stock standard solution with distilled water. Phosphate buffers of pH 3.0 and 7.0, acetate buffer of pH 5.0 and ammonia buffer of pH 8.36 were used.

A 0.1% w/v of chelating agent 4-(2-thiazolylazo resorcinol) (TAR) was prepared in ethanol/water on daily basis which purchased from (E. Merck, Dermstadt, Germany). TMDA 64.2 certified reference material was used. DPCP was used as solid-phase extractor and prepared according to the literature [27].

2.2. Instruments

A Perkin Elmer Model 3110 flame atomic absorption was used for determination of Cu and Zn with the mode of air/acetylene flame. The hollow cathode lamp was used as radiation source and operated at recommended current. The operating parameters for studied metals were set as recommended by the manufacturer. The calibration curves for Cu (0.5–5.0 mg/L) and Zn (0.1–1.0 mg/L) were established by using of working standard solutions. A model Nel pH 900 (Ankara-Turkey) pH meter equipped with a combined glass electrode was used for the pH adjustment of sample solution.

2.3. SPE procedure

Thirty mL of model sample solution containing analyte ions was added to 4.0 mL of phosphate buffer for adjustments of pH at desired pH 7.0. After adjusting pH, 750 µL of 0.1% chelating agent TAR was added. After that the sample solution was passed gravitationally into the column that contains 100 mg of diethylamine-modified phosphorus-containing polymer before washing with distilled water and conditioning with buffer solution of desired pH. The metal ions were retained into the column and were eluted with 3.0 mol/L of nitric acid. Analytes were determined by using FAAS.

2.4. Analysis of water samples

The method was applied to natural water samples. Then the same procedure given in "SPE procedure" section was applied. Analytes were determined by using FAAS.

2.5. Optimization strategy used in experimental design

The experimental data were evaluated with the aid of computer program Excel, Minitab 13.2 (Minitab Inc., State College, PA) and STATISTICA [29]. Optimization was carried out in two steps; first one was PBD and second one was CCD design. PBD design was used for the screening of main variables that influence SPE of Cu and Zn. For the evaluation of four factors including pH, ligand volume (LV), eluent concentration (EC), and eluent volume (EV) two levels were selected at low (−) and high (+) as given in Table 1. A PBD design matrix is shown in Table 2, where significance of the effects was checked by analysis of the variance (ANOVA) and using standardized effect of factors at (0.05) p-values. This optimization method permits estimation of the principal effects of the variables optimized against the % recovery of Cu and Zn. The effect of factors and their interactions can be visualized by Pareto chart as depicted in Fig. 1 for copper and Fig. 2 for zinc.

Table 1
Factors and levels used for the Plackett–Burman and central composite designs in factorial design

Variables	Low (−)	High (+)
pH (P)	3.0	7.0
Ligand volume (LV), μL	100	750
Eluent volume (EV), mL	5.0	10
Eluend concentration (EC), mol/L	1.0	3.0

Table 2
Plackett–Burman design

					% Recovery	
Run	A, pH	B, LV	C, EV	D, EC	Cu(II)	Zn(II)
1	+	−	−	−	69.6	62.8
2	+	+	−	−	79.5	76.8
3	+	+	+	−	82.1	84.0
4	+	+	+	+	100.0	98.9
5	−	+	+	+	50.7	58.5
6	+	−	+	+	88.0	73.4
7	−	+	−	+	52.0	56.6
8	+	−	+	−	77.6	67.0
9	+	+	−	+	81.6	79.8
10	−	+	+	−	43.6	56.6
11	−	−	+	+	65.3	54.3
12	+	−	−	+	75.0	69.1
13	−	+	−	−	41.8	56.5
14	−	−	+	−	46.8	49.3
15	−	−	−	+	58.7	57.6
16	−	−	−	−	45.6	39.9

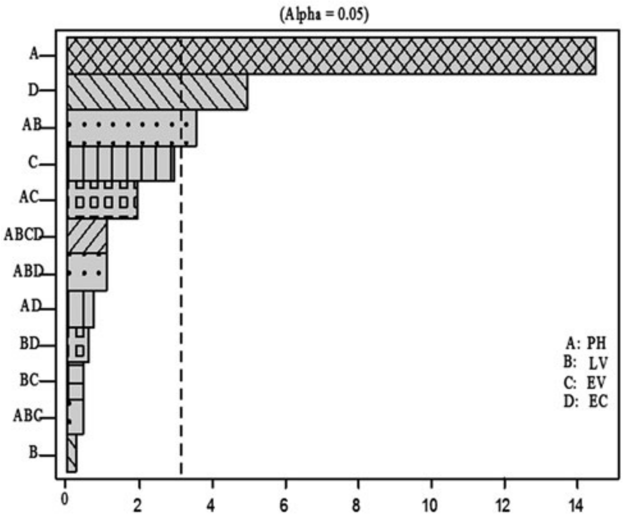

Fig. 1. Pareto chart of effects vs. % recovery of Cu(II).

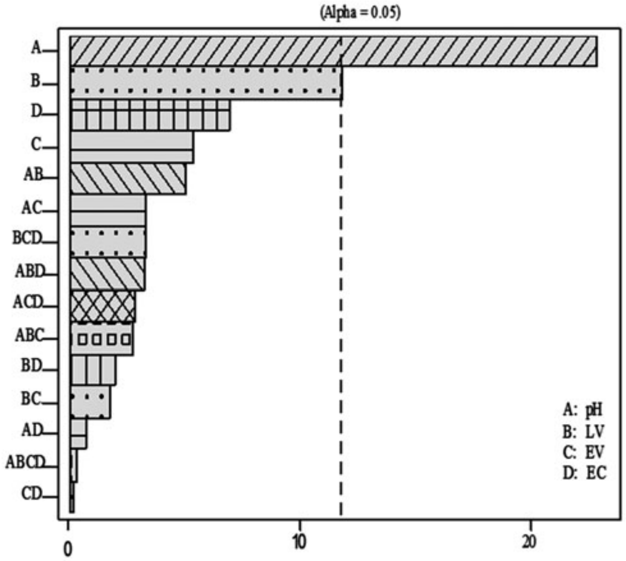

Fig. 2. Pareto chart of effects vs. % recovery of Zn(II).

The evaluations of interactions between the factors were also important, while the effects of some factors were less significant. Moreover, the effects of significant factors were evaluated by CCD to provide the maximum metal recovery. A CCD design with six degrees of freedom and involving 16 experiments were performed to optimize the most significant

Table 3
Central composite design ($n = 6$) for the % recovery of Cu(II) and Zn(II) vs. pH, LV, and EC

				% Recovery	
Run	A, pH	B, LV	C, EC	Cu(II)	Zn(II)
1	−	−	−	30.7	32.6
2	+	−	−	50.7	55.6
3	−	+	−	35.5	30.3
4	+	+	−	75.6	72.3
5	−	−	+	58.2	58.5
6	+	−	+	70.3	65.3
7	−	+	+	59.5	57.3
8	+	+	+	98.7	100.0
9	$-P^1$	F^0	S^0	35.1	25.5
10	$+P^2$	F^0	S^0	30.7	38.5
11	P^0	$-F^1$	S^0	40.3	36.7
12	P^0	$+F^2$	S^0	45.2	53.6
13	P^0	F^0	$-S^1$	52.6	52.5
14	P^0	F^0	$+S^2$	72.2	70.5
15	P^0	F^0	S^0	69.3	68.4
16	P^0	F^0	S^0	69.1	68.4

Note: $-P^1 = -1.682$, $+P^2 = 8.36$, $P^0 = 5.0$, $-F^1 = -122$, $F^0 = 425$, $F^2 = 972$, $-S^1 = -1.682$, $+S^2 = 3.68$, $S^0 = 2.0$.

variables i.e. pH, LV, and EV for the determination of Cu and Zn as summarized given in Table 3. The application of this experimental design reduced the development time of the methods and provided less ambiguous digestion conditions, hence the facilitating data interpretation.

3. Results and discussion

3.1. Optimization of PBDs

In order for the optimization of proposed SPE method, PBD and CCD designs were carried out for the preconcentration of Cu and Zn. In PBD design, four factors including pH, LV, EC, and EV were selected at two levels low (−) and high (+) as described in Table 1. However, in the present study, 16 experiments were performed to explore the main variables influencing on the extraction efficiency. The design matrix and analytical response as a % recovery of metal ions as summarized in Table 2 and their interactions can be visualized by Pareto chart using standardized effect (Figs. 1 and 2).

3.2. Optimization by CCD

The results of factorial design demonstrated that the variables i.e. pH, LV, and EC were selected for final optimization. A CCD with six degrees of freedom involving 16 experiments were performed at three levels for each variables; pH at (3, 5, and 7.0), LV of (100, 425, and 750 μL), and EV of (1.0, 2.0, and 3.0 mL) for the estimation of the response surface methodologies. Thus, a CCD design involving these three significant variables were optimized for the estimation of Cu and Zn and their interactions were studied by response surface methodology (RSM) as shown in Figs. 3 and 4 for copper and Figs. 5 and 6 for zinc. The quantitative recovery of Cu and Zn was obtained at the corresponding values are [P] = 7.0, [LV] = 750 μL, and [EC] = 3.0 mol/L.

3.3. Estimated effects of variables

Optimization of proposed method for preconcentration of Cu and Zn, the four variables were inspected by PBD design as shown in Table 2. In this design, 16 runs have been performed vs. % recovery of Cu and Zn. However, in the view of PBD matrix and Pareto chart, the most significant effect was found for factors i.e. pH, LV, and EC. The three factors were at high level, recoveries were found 100% for Cu and 98.9% for Zn, respectively as shown in experiment 4, while EV was at low level.

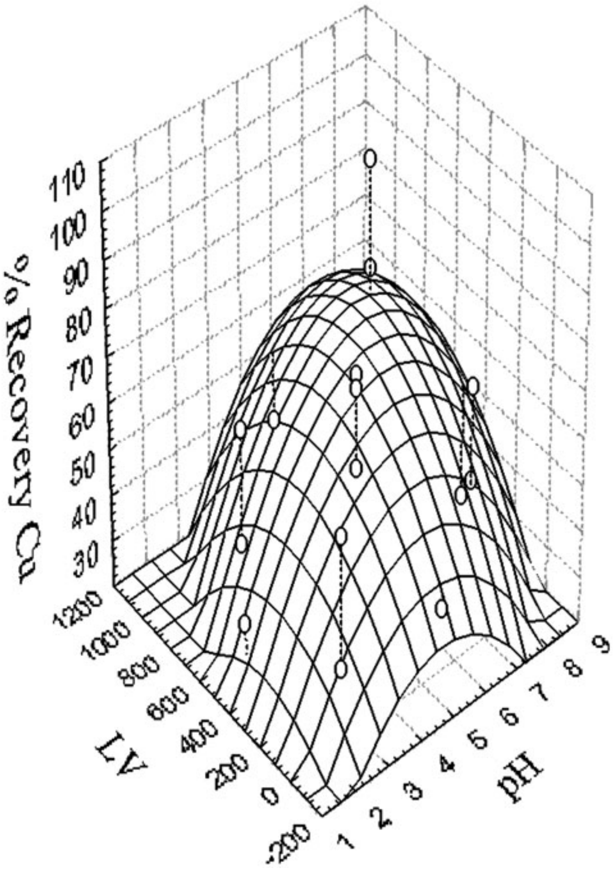

Fig. 3. 3D surface response for % recovery of Cu vs. pH and LV.

From the results of the PBDs and CCD (Tables 2 and 3), it was clearly seen that the high pH (+) provided a significantly high recovery for Cu(II) and Zn (II) as compared to rest of the factors i.e. LV, EC, and EV. pH plays a very important role in metal chelate formation and the consequent extraction [30–36]. The experimental results showed that pH is one of the most significant factors in the optimization of experimental conditions. The results showed that the analytical signal of metal ions was increased by increasing the pH (experiment 1), whereas the remaining factors were at low (−) level. % Recoveries were observed for Cu is 69.6 and for Zn is 62.8. In experiment 5, % recovery 50.7 for Cu and 58.5% for Zn were obtained low at low (−) pH 3 and whereas rest of the factors were at high level (+) as summarized in Table 2. The effect of significant variables and their interactions were evaluated by Pareto chart as shown in Fig. 1 for copper and in Fig. 2 for zinc.

Thus, the three most significant factors such as pH, LV, and EC were to be further optimized by central composite design. A CCD was used for sequential

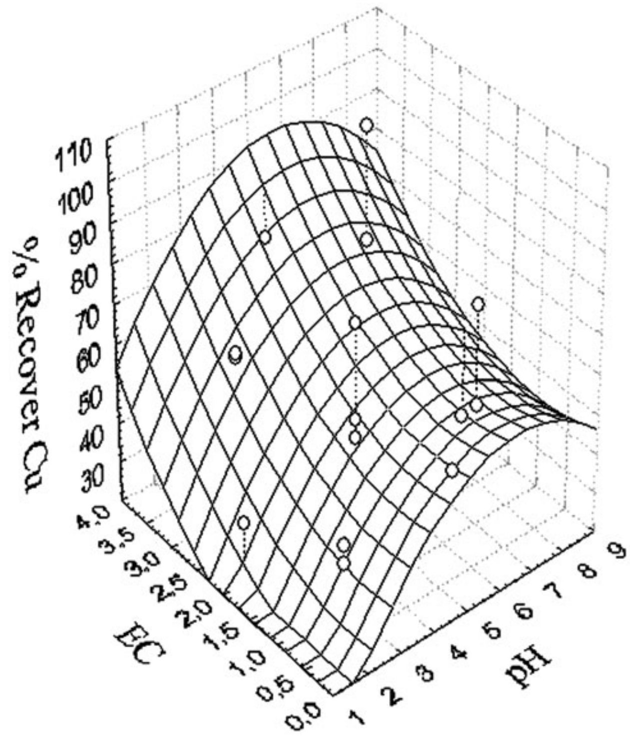

Fig. 4. 3D surface response for % recovery of Cu vs. pH and EC.

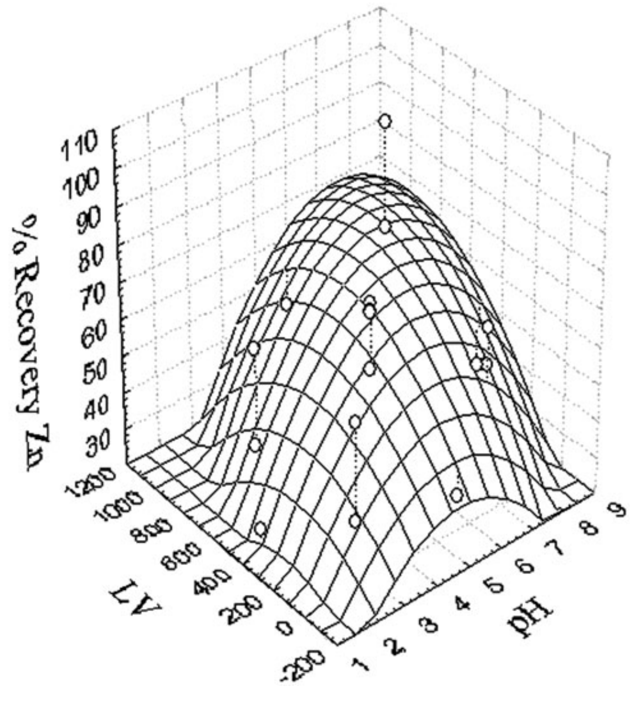

Fig. 5. 3D surface response for % recovery of Zn vs. pH and LV.

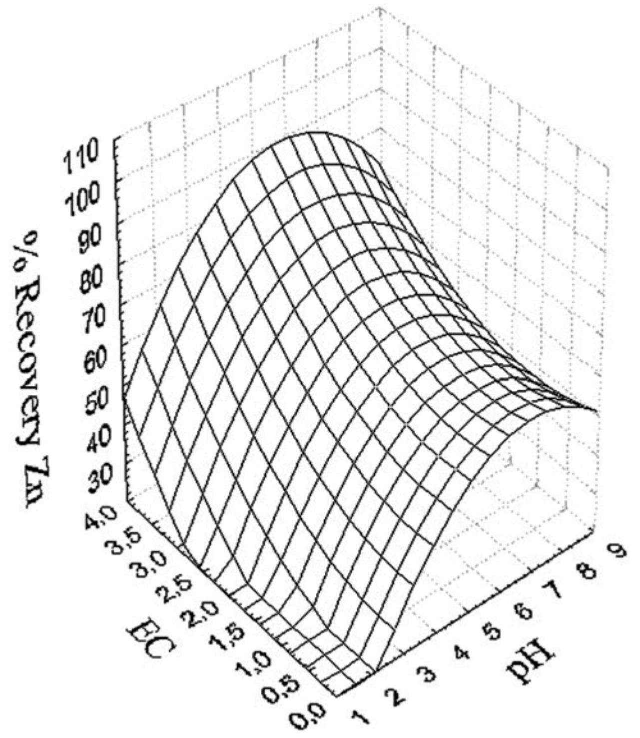

Fig. 6. 3D surface response for % recovery of Zn vs. pH and EC.

experimentation and gives the reasonable information that factors are more influencing on the response. In experiment 2, all three selected factors were found at low level; hence low % recoveries were observed: 50.7 for Cu and 55.6% for Zn.

Eluent concentration and pH were at minimum level and while ligand volume were at high level, but % recovery of both metal ions were low as can be seen in experiment 3. On the other hand, when pH and EC were at maximum level (experiment 6) and % recovery was achieved for Cu (70.3%) and for Zn (65.3%), respectively. The results indicated that maximum

Table 4
Effects of foreign ions

Foreign ions	Tolerance limit (mg/L)
Ca^{2+}	3,000
Mg^{2+}	3,000
Na^{+}	2,000
K^{+}	2,500
PO_4^{3-}	1,000
NO_3^{-}	2,000
SO_4^{2-}	2,000
Pb^{2+}	25

Table 5
Determinations of Cu and Zn in TMDA-64.2 water CRM μg/L ($N = 6$)

Metals	Experimental value $\bar{x} \pm ts/\sqrt{n}$[a]	Certified values $\bar{x} \pm ts/\sqrt{n}$[a]	% Recovery[b]	Paired *t*-test *T*-critical[c]
Cu	275 ± 9	274	100	0.021
Zn	315 ± 19	310	102	0.22

[a] Mean ± standard deviation.

[b] % Recovery = [Experimental value / Certified value] × 100.

[c] *T*-critical = 2.571 (df = 5, $N = 6$).

Table 6
Level of copper and zinc in water samples (μg/L)

Water samples	Cu	Zn
Tap water	5.54 ± 0.26	BDL
Bottled mineral water	4.46 ± 0.23	BDL

Note: Mean of three determinations ± standard deviation.
BDL: Below the detection limit.

extraction efficiency of 98.7% were achieved for Cu and 100% were achieved for Zn (in experiment 8). Among the three variables, only one variable was fixed at the central points and the remaining two variables are allowed to vary as shown in Figs. 3 and 4 for copper and Figs. 5 and 6 for zinc. The plot of each pairs of variable was depicted as (pH and LV), and (pH and EC) vs. % recovery of Cu(II) and Zn(II).

3.4. Interferences study

The possible effects of some anions and cations on the flame atomic absorption spectrometric determination of transition metals are known as matrix effects [37–41] and they are very problematic in the solid-phase extraction studies. The influence of matrix ions on % recovery of Cu(II) and Zn(II) was studied. The solutions containing analyte ions and different concentrations of alkaline, alkaline earth, and some metal ions were prepared separately and were applied the preconcentration procedure (Table 4). It was clearly seen that the common coexisting ions did not have any significant effect on the preconcentration/separation and determination of understudy metal ions. The proposed method was free from foreign-interfering species.

3.5. Analytical figure of merit

The analytical figures of the developed procedure were evaluated. Intraday and interday relative standard deviation values for analytes were less than 1.9 and 3.3%, respectively. The calibration graph was established using standard solutions of Cu and Zn in water. The limit of detection is defined as 3 s, where s

Table 7
Comparison of the preconcentration procedures with presented method

Technique	System	Detection system	DL (μg/L)	Ref.
SPE	Amine-functionalized graphene nanosheet	FAAS	Cu: 0.05 Zn: 0.1	[42]
SPE	Calmagite–Amberlite XAD-1180 resin	FAAS	Cu:1.98	[43]
SPE	Multiwalled carbon nanotube modified with (3-mercaptopropyl) silanetriolate	FAAS	Cu: 1.6 Zn: 1.4	44]
SPE	Palladium nanoparticles attached to silica gel chemically bonded by silica-bonded N-propylmorpholine	FAAS	Zn: 1.4	[45]
Ionic liquid-based dispersive liquid–liquid microextraction	1-(2-thenoyl)-3,3,3-trifluoracetone	ICP-OES	Cu: 0.1 Zn: 0.1	[46]
SPE	Diethylamine-modified phosphorus-containing polymer/4-(2-thiazolylazo) resorcinol	FAAS	Cu: 2.1 Zn: 6.3	This work

Note: FAAS: flame atomic absorption spectrometry, ICP-OES: inductively coupled plasma-optical emission spectrometry, SPE: solid-phase extraction, DL: detection limit.

is the standard deviation of 10 measurements of blank readings, were found 2.1 μg/L for Cu, and 6.3 μg/L for Zn, respectively. The preconcentration factor was 50 with a sample volume of 100 mL and an eluent volume of 2 mL. The consumptive index (CI) can be found for practical purposes as: CI = Vs/EF where Vs is the volume of sample solution (mL) consumed to achieve the EF value. The CI was found 2.0 m/L.

3.6. Analytical application to real samples

The accuracy of the proposed method was checked by the analysis of certified reference material (CRM) samples TMDA-64.2, as given in Table 5. The determined values were found in good agreement with the certified values at 95% confidence limit.

The procedure was also applied to determine the Cu and Zn from natural water samples. The results of water samples are shown in Table 6. On the basis of results, it was concluded that the applicability and reproducibility of our developed methodology was reliable and free from foreign ions, and also can be successfully applied to environmental samples.

4. Conclusions

The SPE procedure for the preconcentration of Cu and Zn in water samples was successfully optimized by multivariate technique. A PBD design was mainly used to determine the influence of a number of factors on a response, and which is important. In order to further optimize, the most significant variables were inspected by central composite design. The estimated values of three significant variables were evaluated by RSM. The application of multivariate technique was rapid and fast means of optimization of significant variables simultaneously. The main advantage of multivariate techniques such as PBD and CCD was applied to fast an efficient and minimum amount of reagents used in the optimization of variables and also can be successfully applied to real samples without matrix interferences. The method is simple, rapid, inexpensive, as well as environmental friendly (Table 7). The proposed method was also free of interference compared with conventional methods used to determine Cu(II) and Zn(II).

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