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ORIGINAL ARTICLE

Preconcentration of Zn(II) Using β-CyclodextrinButanediolDiglycidyl Ether Polymer Modified With 1-(2-Pyridylazo)-2-Naphthol) (PAN)

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ABSTRACT

In this study, a solid phase extraction method has been developed for the preconcentration of Zn(II) at trace level using β-cyclodextrin polymer modified with 1-(2-Pyridylazo)-2-Naphthol (PAN) reagent. After preconcentration, metal retained on the polymer was eluted with 5.0 mL of 2.0M HCl and then determined by UV-VIS spectrophotometry. The factors affecting the preconcentration of the Zn(II) such as pH, concentration of the eluent, eluent volume and matrix components were also ascertained. The recovery of Zn(II) was found to be ≥ 95% and preconcentration factor was found to be 70. The relative standard deviation of the method was 1.0%. The analytical detection limit was found to be 2.06 ng/mL.The proposed method has been applied for the determination of Zn(II) in different water samples and certified alloy samples.

Keywords:*β-cyclodextrin polymer, Zn(II), preconcentration, 1-(2-Pyridylazo)-2-Naphthol*

1. INTRODUCTION

The industrial use of metals leads to increase of metal concentrations in air, water and soils. Metals are nonbiodegradable and nonthermodegradable, thus, are accumulated by living organisms.Therefore, separation of these metals in samples at micro and trace levels is of paramount importance in the context of environmental protection, food and agricultural chemistry and high purity material development. In spite of the inherent high sensitivities obtained for techniques like ETAAS [1], ICP–OES [2], ICP–MS [3], GFAAS [4], ICP-AES [5], used for the determination and preconcentration of Zn(II), are relatively expensive, requires the use of the high experts and present some limitations related to the concomitants such as high dissolved solid contents of samples. Therefore, it is evident that despite recent advances in analytical instrumentation, the use of separation and or preconcentration procedures is still necessary before the determination step.Different techniques are used for the separation and preconcentration of metals in the solution. Theseinclude liquid-liquid extraction [6], cloud point extraction [7], electrochemical deposition [8] and solid phase extraction [9]. Disadvantages such as significant chemical additives, solvent losses, complex equipments, large secondary wastes,prefiltration problems and time consumingprocedures, limit the application of most of these techniques. Solid phase extraction, however, solves this problem as it offers several advantages. These include: (1) high enrichment factors; (2) short extraction times; (3) minimal costs due to low consumption of reagents; (4) absence of emulsion; (5) ease of automation; (6) safety with respect to the hazardous samples; (7) high selectivity. This technique is also attractive as there is no need to use organic solvents, which may cause potential

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[♠] Correspondingauthor, e-mail: jaggisandeep@ymail.com toxic effects. Activated carbons [10], silica nanoparticles [11], banana peel [12], carbon nanotubes [13], agricultural adsorbents [14] etc. have been employed to preconcentrate different analytes as the SPE sorbents. Supramoleculer chemistry with β-Cyclodextrin has been a very active research field in the past few years [15-17]. β-Cyclodextrin (β-CD) is a very stable oligosaccharide that is composed of seven glucose units linked with each other by α-(1,4)-glycosidic linkage. It can form supramoleculer complexes with several organic compounds by incorporating them into their hydrophobic cavities. When two or more β-cyclodextrinare covalently linked with each other they are known as the polymers. These β-cyclodextrin polymer have been used for the preconcentration of various analytes [18-21]. Till date author find no report of the use of β-CyclodextrinButanediolDiglycidyl Ether Polymer (β-CDBP) modified with PAN for the preconcentration of the metal ions. It was therefore, thought worth while to prepare a chelating resin by immobilizing PAN on β-CDBP and use it in the preconcentration of Zn(II).

2. MATERIALS AND METHODS

2.1. Chemicals and equipments

All reagents used were of analytical reagent grade. Double distilled water was used throughout the experiment. Zn(II) solution was prepared by dissolving 0.287gof Zinc sulphateheptahydrate [$ZnSO_4.7H_2O$] in 100ml of distilled water to give standard stock solution. 4×10^{-6}mol/L solution of the PAN reagent was prepared by dissolving an appropriate amount of PAN (Fluka Chemical Company) in N,N-dimethylformamide solvent. 1,4-Butanediol diglycidyl ether was obtained from sigma Aldrich chemical company (U.S.A.). β-Cyclodextrin was obtained from SD fine chemical India private limited (Mumbai). Buffer solution used were hydrochloric acid/ sodium acetate for pH 2.0-3.5, sodium acetate/acetic acid for pH 4.0-6.5, ammonia/ammonium chloride for pH 8-11. Glass wares were washed with chromic acid and soaked in 5% nitric acid and rinsed with double distilled water.A Shimadzu UV-1800 spectrophotometer (Shimadzu Ltd., Japan) equipped with the matched 10-mm quartz cells was used to measure absorbance. All pH measurements were performed using Digital century pH-meter CP 901 with a combined glass electrode. A thermostatic shaking water bath (Perfit India Ltd.) was used to carry out all the inclusive procedures.

2.2. Procedure

2.2.1. Synthesis of the β-Cyclodextrinbutanedioldiglycidyl ether polymer (β-CDBP)

β-CDBP was synthesized by known method [22]. A brief procedure for the synthesis is mentioned here. 20g of β-CD was dissolved in 50ml of 20% NaOH. To this was added 20ml of butanedioldiglycidyl ether drop wise. The polymer was formed in 1.5h and dried at 90^0C at 1 atm. pressure. The polymer was ground and sieved into 40-60, 60-80, 80-100 and over 100 mesh fractions. The 80-100 mesh fraction was washed with double distilled water 5-6 times. Then, the polymer was dried again at 90˚C and kept at room temperature (25˚C) in a dessicator.

2.2.2 Inclusion of the PAN in the β-CDBP cavity to form β-CDBP-PAN modified polymer

5.0g of the synthesized polymer, β-CDBP (80-100) mesh size was taken in a 250ml stoppered conical flask. To this was added 10ml of 9.5 pH buffer solution and polymer was allowed to swell for 15 minutes. A fixed volume of 4×10^{-6}mol/L solution of the PAN was added to the treated polymer and made 50ml with distilled water. It was shaken for two hours. The colored polymer so obtained was washed with distilled water and dried at 100˚C at 1atm pressure. The modified polymer was stored in a dessicator at room temperature for future use.

2.2.3. Batch extraction procedure

At room temperature i.e., 30^0C β-CDBP-PAN (500mg) and 10.0 ml of buffer solution (pH 9.5) were added to a 100-ml stoppered conical flask. The mixture was allowed to stand for approximately 15 min so that β-CDBP-PAN could be swollen sufficiently. 100 ng/mL of Zn(II) was added and made up to 100ml with double distilled water. After the mixture was shaken in the thermostatic shaking water bath for 45 min, 5.0ml of the supernatant solution was transferred into a 10ml volumetric flask and the absorbance was measured using standard spectrophotometric method [23].

2.2.4. Elution of the Zn(II)

Zn(II) retained on β-CDBP-PAN polymer was eluted using 5.0 mL of 2M HCl. Eluted Zn(II) was determined using standard spectrophotometric method [23].

2.2.5. Regeneration of the polymer

The polymer was regenerated by dipping it in the 10.0% TX-100 (w/v) for 1h and then washing with distilled water; β-CDBP was further treated with HNO_3 and was finally washed with distilled water to neutral conditions.

2.2.6. Sample Collection and Conditioning

Water samples were collected from the different parts of Patiala City. The water samples were immediately filtered through cellulose membrane filter (0.45nm pore size), and stored in precleaned polyethylene bottles. After then, pH of the sample was adjusted to 9.5 and the preconcentrtion procedure as described above was applied.

2.2.7. Determination of Zn(II) in standard alloys

The accuracy of the proposed method was verified by the determination of Zn(II) in standard reference alloy samples. A 0.1 g of the standard alloy was completely dissolved in 20mL of hydrochloric acid by heating on a water bath; 2ml of 30%(w/v) hydrogen peroxide was added to the solution. The excess of peroxide was decomposed by heating the solution on a water bath. The solution was cooled, filtered and diluted to 100 ml with An aliquot of this solution was taken and preconcentration was done by the developed procedure.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The complexationof the metal ion with PAN on the chelating resin is dependent on the pH of sample solution due to the competitive reaction between chelate forming groups and hydrogen ions in the solutions. 100 ng/mL of Zn(II) were spiked to a 100 mL of the model solution. The pH of this solution was adjusted in the range of 2.5 to 10.5 using different buffer solutions and then the preconcentration procedure as described was applied. As it can be seen in (Figure 1), quantitative uptake (≥ 95%) was obtained at pH 9.5 and above. Therefore, the working pH was chosen as 9.5 for the subsequent experiments.

double distilled. Further dilutions were made as required.

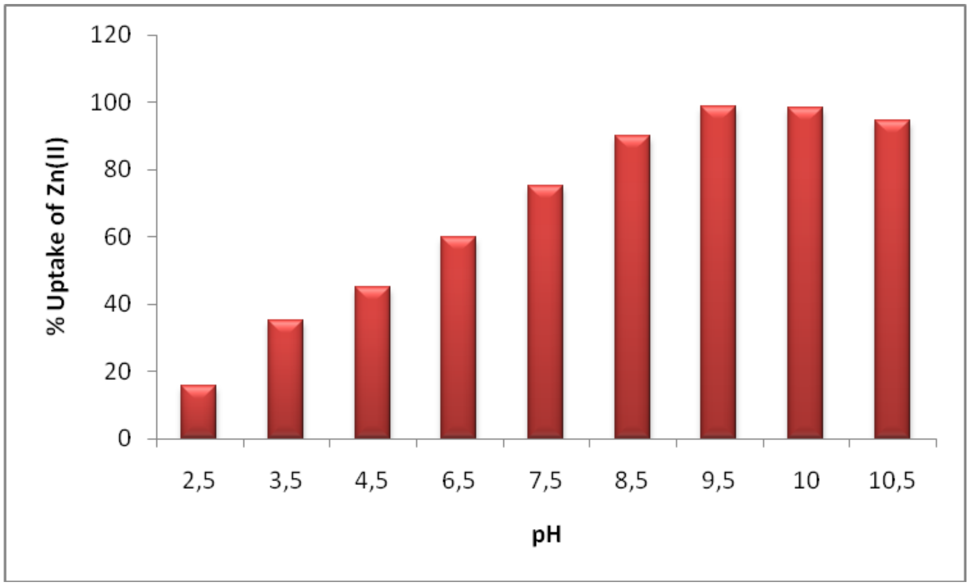

Figure 1.Effect of pH on the % uptake of Zn(II)

3.2 Effect of the amount of adsorbent (Bed Height)

The amount of the resin is another important parameter that affects the uptake. A quantitative retention (≥ 95%) cannot be achieved when the resin is less than the optimum amount. On the other hand, an excess amount of resin prevents the quantitative elution of the retained metal chelate by a small volume of the eluent.In order to optimize the smallest amount ofextractant, 100, 200, 300, 400, 500, 600 and 700mg of the resin were added to the same volume of the synthetic solution containing 100 ng/mL of Zn(II) and preconcentrated by the general procedure. The quantitative recoveries were obtained for and above 500 mg of resin (Figure2). Therefore, 500 mg of the resin has been used for subsequent experiments.

3.3 Effect of shaking time

Shaking time is an important factor in determining the possibility of application of the β-CDBP-PAN polymer for the selective uptake of Zn(II). Different shaking time (ranging from 15 to 75min) were studied for the % uptake of Zn(II) by β-CDBP-PAN polymer. The results of % uptake of Zn(II) vs. the shaking time show that the percentage uptake reach maximum (above 95%) at 45 min (Figure 3). Therefore, the shaking time of 45 min. was selected as the adsorption equilibrium time.

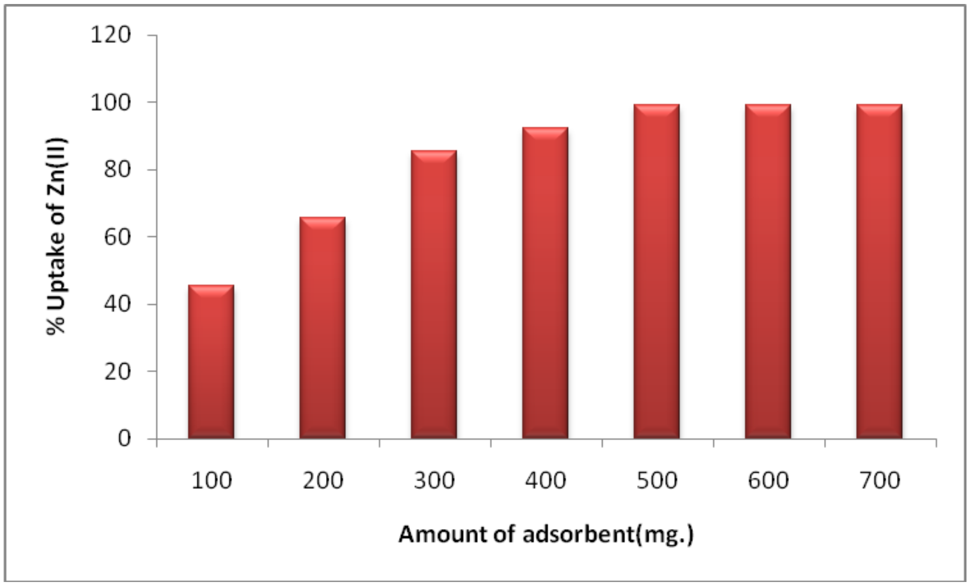

Figure 2.Effect of the amount of adsorbent on the % uptake of Zn(II)

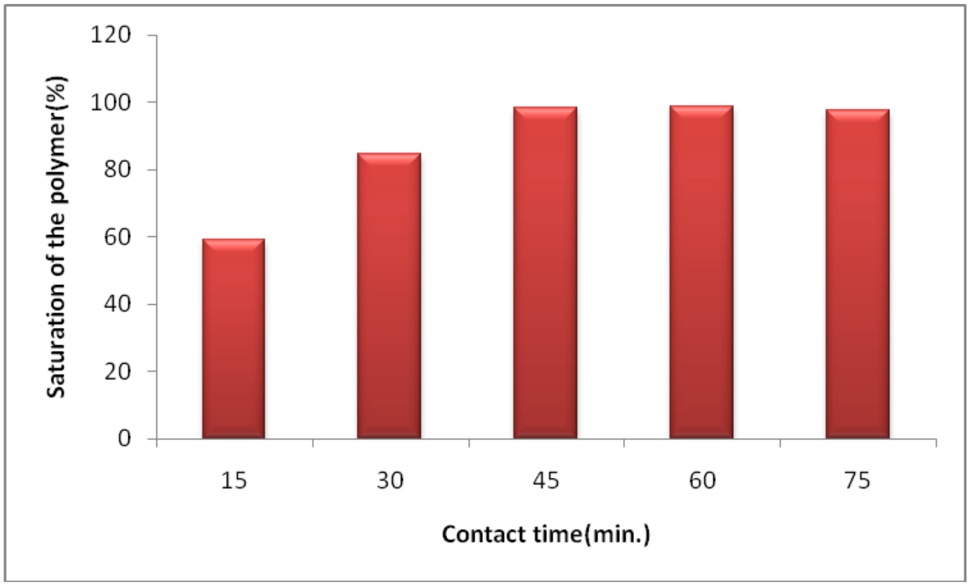

Figure 3.Effect of the contact time on the % uptake of Zn(II)

3.4 Effect of the Mesh Size of the β-CDBP-PAN Polymer

Mesh size of the polymer is an important factor that affects the % uptake of the ions from the sample solution so the effect of the mesh size of β-CDBP-PAN polymer on the % uptake of Zn(II) was also studied. For this purpose, polymers of the various mesh size were used under optimal conditions (pH, shaking time, sample volume, etc.). Quantitative uptake of Zn(II) (above 95%) was achieved using the polymer of the mesh size of 80-100 and above 100 (Figure4). Therefore, 80-100 mesh size of the polymer was chosen for further experiments.

3.6 Effect of the sample volume

In order to explore the possibility of enriching low concentration of analytes from large volume of solution, the effect of sample volume on the retention of Zn(II) ion was also investigated. For this purpose, 25, 50, 100, 150, 200, 250, 300, 350, 400 and 450 mL of sample solutions containing 100 ng/mL of Zn(II) were taken. Quantitative uptakes (≥ 95%) wereobtained for sample volume of ≤350 mL (Figure5). Therefore, 100 mL of sample solution was adopted for the preconcentrtion of analyte from sample solutions. The preconcentration factor was 70 when eluent volume is 5.0 mL.

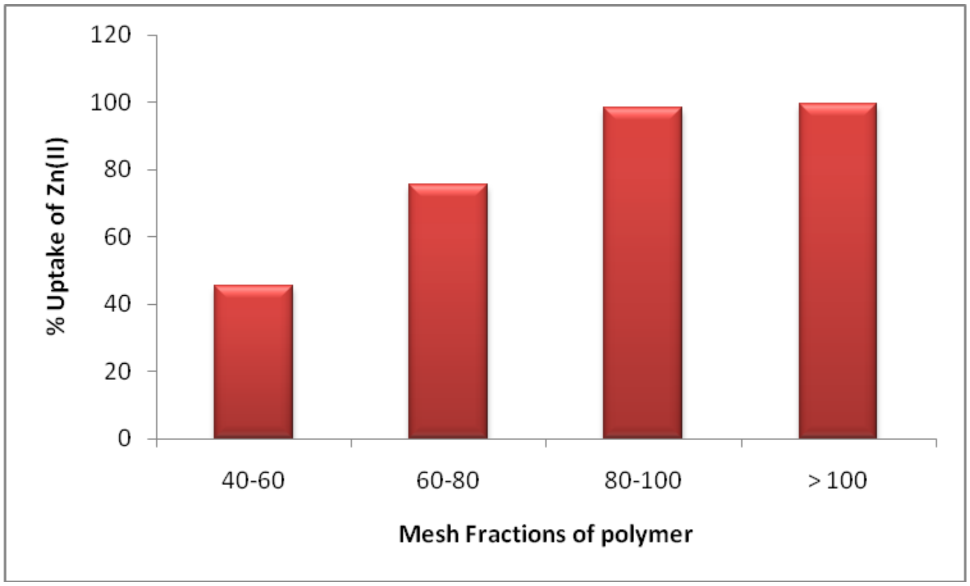

Figure 4. Effect of mesh fractions of the polymer on the % uptake of Zn(II)

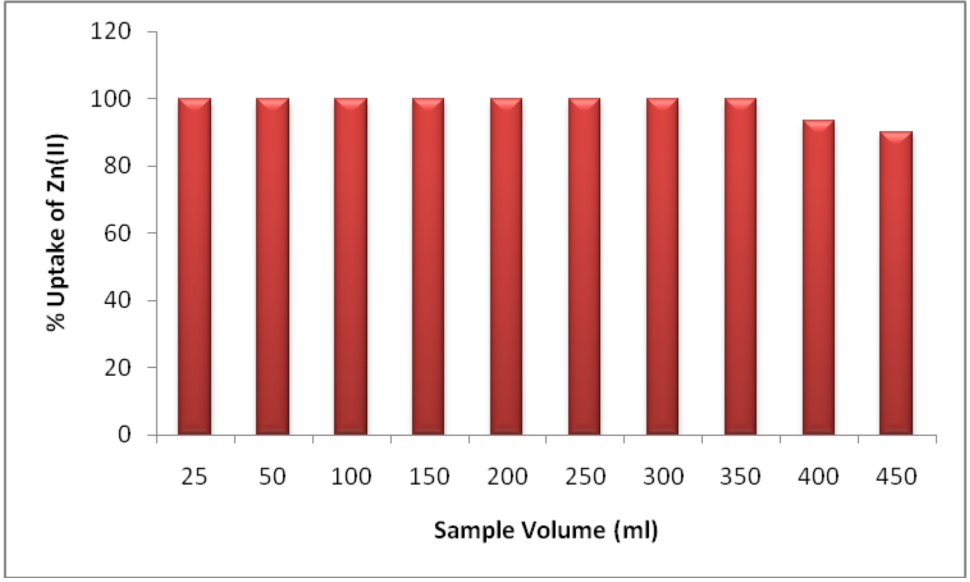

Figure 5. Effect of the sample volume on the % uptake of Zn(II)

3.8 Effect of elution conditions on recovery

Since the adsorption of Zn(II) at pH ≤ 2 is quite low, one can expect that elution will be favored in the acidic solutions. So various concentrations and volumes of HCl were used for the desorption of retained Zn(II). The experimental results showed that 2M HCl was sufficient for complete elution of Zn(II) (Figure6). It was found that quantitative recoveries (≥95%) with 5.0 mL of 2.0M HCl as eluent could be obtained (Figure7). Therefore, for eluting Zn(II) 5.0 mL of 2.0M HCl was used as eluent.

3.9 Matrix Effects

Synthetic solutions containing 100 ng/mL of Zn(II) and various amounts of foreign ions were prepared and general procedure was followed. The tolerance limit was defined as the amount of foreign ions causing a change less than 5% in the recovery of Zn(II). Table 1. Shows the results, as can be seen a very good selectivity is achieved.

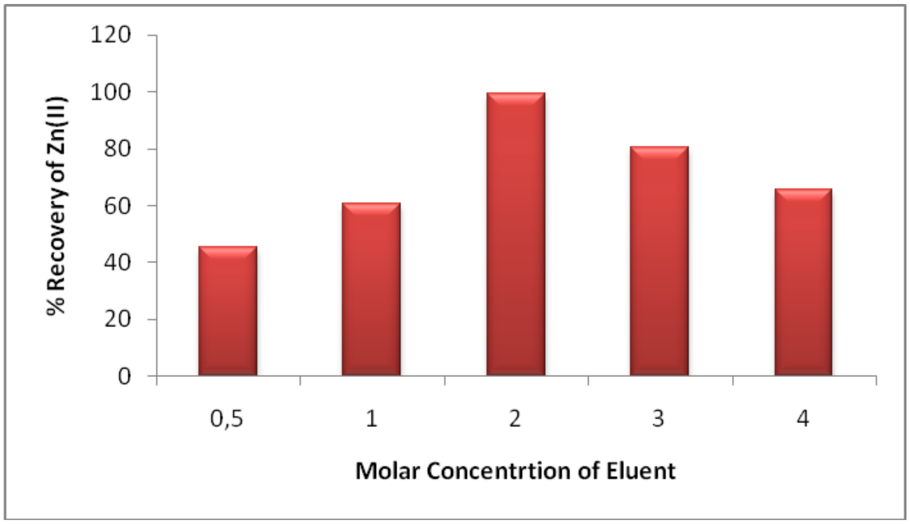

Figure 6. Effect of molar concentration of eluent on the % recovery of Zn(II)

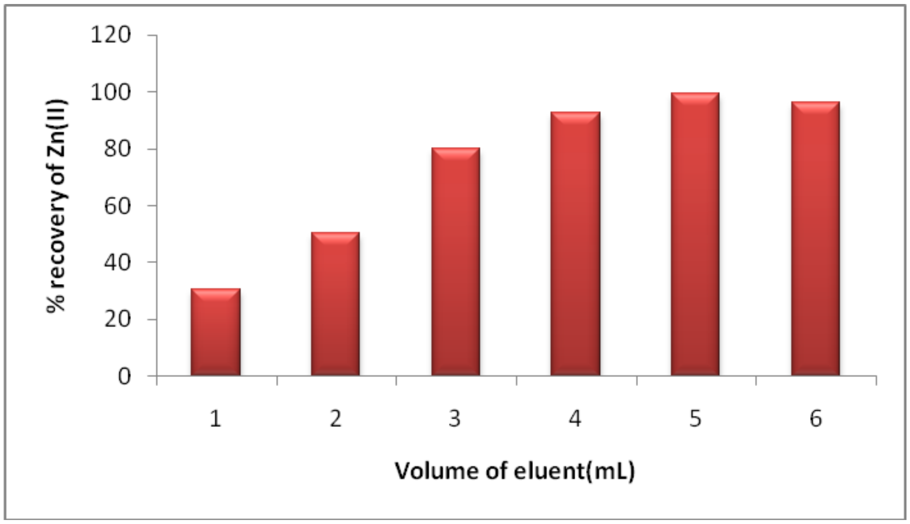

Figure 7. Effect of eluent volume on the % recovery of Zn(II)

Table 1.The effect of foreign ions on the determination of 100 ng/mL of Zn(II) (n=3)

Foreign ions	**Tolerance limit[$W_{Foreign\ ion}/W_{Zn(II)}$]**
NO_3^-, SO_4^{2-}, HPO_4^{2-}, SCN^-, NO_2^-, PO_4^{3-}	>1000
Na^+, K^+, Mg^{2+}, Ba^{2+}, Al^{3+}, Rb^+, Cs^+, Ag^+	1000
Sb^{3+}, Ca^{2+}, Zr^{4+}, Ti	500
Th^{4+}, Sn^{2+}, As^{3+}	100
$^aFe^{3+}$, $^bNi^{2+}$, $^cCu^{2+}$, $^dCo^{2+}$	10
$^eHg^{2+}$, $^eCd^{2+}$, $^fPb^{2+}$, $^gFe^{2+}$, $^hMn^{2+}$	1
EDTA, Br^-, F^-, CN^-, citrate	1

a-masked with 1.0 mL of 5.0% ammonium oxalate solution; **b**-masked with 1.0 mL of 2.0% dimethylglyoxime; **c**-masked with 1.0 mL of 3.0% sodium thiosulphate; **d**-masked with 1.0 mL of 10.0% α-benzilmonoxime; **e**-masked with 5.0 mL of 2.0% sodium thioglycollate solution; **f**- masked with 2.0 mL 0f 1.0% sodium sulphate solution; **g**-masked with 1.0 mL of 2.0% 1,10-phenenthroline; **h**-masked with 2.0 mL 3.0% sodium hexametaphosphate solution.

Table 2.Various parameters studied for the preconcentration of Zn(II) using β-CDBP-PAN polymer as extractant

Serial No.	**Parameters**	**Zn(II)**
1.	pH	9.5
2.	Contact Time(min.)	45
3.	Sample Volume(mL)	100.0
4.	Particle Size	80-100
5.	Adsorbent Dose(mg.)	500
6.	Eluent Concentration(M)	2.0
7.	Eluent Volume(mL)	5.0
8.	Preconcentration Factor	70

4.Applications and accuracy of the method

The method was applied to the determination of Zn(II) in water samples and certified alloy samples. The results are given in the table 3 and 4 respectively. The accuracy of the described preconcentration method was tested in the recovery studies by adding known amounts of the metal ion to the water sample and also by analysis of the certified alloy samples. The results obtained from the analysis of water samples and certified alloys, are depicted in (Table 3,4) respectively. The recovery values obtained from the water and alloy samples were satisfactory. These results confirm the validity of the proposed method.

Table 3.Determination of Zn(II) in differentwater samples (n=3)

Water Samples	**Spiked(ng/ml) Zn(II)**	**Found(ng/ml) Zn(II)**	**% Relative Error**	**% Recovery**
Tap water	0.0 70.0 55.5	25.0 94.7 80.3	---- 0.4 0.4	------ 99.6 99.6
Rose water	0.0 50.0 40.0	N.D. 50.5 40.6	----- -1.0 -1.5	------ 101.0 101.5
Bore water	0.0 60.0 70.0	15.6 75.4 85.3	----- 0.3 0.4	------- 99.7 99.6

N.D. not detected

Table 4.Determination ofZn(II) in certified alloy samples (n=3)

Alloy Sample	**Certified Composition**	**Present(ng/ml) Zn(II)**	**Found(ng/ml) Zn(II)**	**% Relative Error**	**% Recovery**
Brass No. 42	Cu 58, Pb 2.56, Zn 38.99, Fe 0.09, Sn 0.12	110 78.0	109.8 77.89	0.18 0.14	99.81 99.85
Zamak-5	Zn 95, Al 4, Cu 1, Mg 0.5	40.0 45.0	39.92 44.85	0.20 0.33	99.80 99.66

6. CONCLUSION

The proposed preconcentration method consists of a simple and low cost procedure which permits the quantitative recovery of Zn(II) from water and certified alloy sample. Based on the high affinity of the modified polymer for Zn(II), the selective determination of Zn(II) is possible. The preparation of the polymer is easy and the method has a good accuracy, sensitivity and repeatability. The modified polymer has been used in all the experiments performed for this study. It has a unique stability and reusability. The RSD of the method was 1%. The recoveries obtained were ≥ 95% in all the cases. The method has a preconcentration factor of 70 and is higher than most of the cited studies in the literature.

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