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Separation of zinc from aqueous samples using a molecular imprinting technique

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In this article, the separation of zinc from aqueous samples by solid-phase extraction based on a molecular imprinting technique is described. Zn-imprinted polymer was prepared by free radical solution polymerisation in a glass tube containing ZnSO₄, morin, 4-vinylpyridine as a functional monomer, ethylene-glycoldimethacrylate as a cross-linking monomer, and 2,2'-azobisisobutyronitrile as an initiator. The obtained polymer block was ground and sieved (55–75 μm) and the Zn–morin complex was separated from polymer particles by leaching with 2M HCl. The synthesised polymer particles have been characterised by IR and differential scanning calorimetric studies either before or after leaching. The effects of different parameters, such as pH, adsorption and desorption time, type and minimum amount of the eluent for elution of the complex from polymer were evaluated. Extraction efficiency more than 99% was obtained by elution of the polymers with 10 mL of CH₂Cl₂–dimethyl sulfoxide (1 : 1, v/v). The detection limit of the proposed method was 2.9 μg L⁻¹. A dynamic linear range in the range of 25–200 μg L⁻¹ was obtained. The relative standard deviation was found to be below 9.2%. In addition, the influence of various cationic and anionic interferences on the complex recovery was studied. The method was applied to the recovery and determination of Zn in a few different real samples.

Keywords: Zn determination; molecular imprinting polymer; morin; separation; water analysis

1. Introduction

Zinc is an essential mineral for sustaining all life. Deficiency of Zn in the human body leads to several disorders, but an excessive Zn intake also causes various acute and chronic adverse effects. Zn has been reported to cause electrolyte imbalance, nausea, anaemia and lethargy. It is a key factor in prostate gland function and reproductive organ growth. It is estimated that 3000 of the hundreds of thousands of proteins in the human body contain Zn prosthetic groups, one type of which is the so-called Zn finger. In addition, there are over a dozen types of cells in the human body that secrete Zn ions,

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and the roles of these secreted Zn signals in medicine and health are now being actively studied. Zn ions are now considered to be neurotransmitters. Cells in the salivary gland, prostate, immune system and intestine use Zn signalling. Zn is also involved in olfaction: the olfactory receptors contain Zn-binding sites and a deficiency of Zn causes anosmia (<http://en.wikipedia.org/wiki/Zinc>) [1,2]. Concentrations above 5 mg L^{-1} can cause a bitter astringent taste and opalescence in alkaline waters.

As the number of ecological and health problems associated with environmental contamination continues to rise, the determination of trace heavy metals in environmental samples is becoming more and more important. Hence, extraction and removal of toxic heavy metal ions from various matrices at trace level are of paramount importance. Due to the very low concentration of most elements like Zn(II) in environmental samples, their separation and sensitive determination necessitate using a preconcentration or trace enrichment method. The classical liquid-liquid extraction is usually time-consuming and labour-extensive and requires relatively large volumes of high purity solvents [3,4].

He *et al.* [5] reported the preconcentration and separation of Zn^{2+} using surface Zn(II)-imprinted functionalised silica gel sorbent. Zhao and co-workers [6] reported the synthesis of Zn(II) ion-imprinted solid-phase extraction material and its analytical application.

Lemaire *et al.* [7,8] developed ion-imprinted resins based on EDTA and DTPA derivatives for the selective separation of Gd from La, Nd, Eu and Lu ions. Uezu *et al.* [9] reported that post-irradiation of imprinted polymer particles by γ -irradiation resulted in better separation of Zn compared with copper. Biju *et al.* [10] reported effect of γ -irradiation of ion-imprinted polymer particles for the preconcentrative separation of dysprosium.

In this study, a molecular imprinting polymer was used for selective extraction and preconcentration of Zn complex from aqueous solution. In synthesis processes, morin, 4-vinylpyridine (VP), ethyleneglycol dimethacrylate (EDMA) and 2,2'-azobisisobutyronitrile (AIBN) were used as Zn complexing reagent, monomer, cross-linker and initiator, respectively. The synthesised polymer was applied for the selective extraction of Zn from aqueous media. The effect of various experimental conditions such as pH, adsorption and desorption time, type and eluent volume on the extraction efficiency were investigated and optimised. The breakthrough volume, dynamic linear range and detection limit were evaluated at optimal experimental conditions.

2. Experimental

2.1 Materials

VP, EDMA and AIBN were obtained from Aldrich (Milwaukee, WI, USA). All acids used were of the highest purity available from Merck (Darmstadt, Germany) and used as received. Reagent grade ZnSO_4 (99.5%) and nitrate or chloride salts of other cations (all from Merck) were used without any further purification. Reagent grade morin (Merck) was used as received. Stock solution of Zn (1000 mg L^{-1}) was prepared by adding the proper amount of ZnSO_4 in double-distilled water in a 50 mL volumetric flask and diluting to the mark with water. Dilute solutions were prepared by appropriate stock solution dilution in double-distilled water.

Table 1. ICP-OES instrumental conditions.

Plasma	Argon
RF generator power (kW)	1.5
Plasma gas flow rate (L min ⁻¹)	15.0
Auxiliary gas flow rate (L min ⁻¹)	1.5
Frequency of RF generator (MHz)	40.0
Observation high (mm)	8.0
Nebuliser pressure (KPa)	240

2.2 Apparatus

The measurements were performed using a simultaneous inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista-Pro, Australia) coupled to a V-groove nebuliser and equipped with a charge-coupled device (CCD). The ICP conditions are shown in Table 1. The pH was determined by a model 630 Metrohm pH meter with combined glass-calomel electrode.

2.3 Preparation of polymer

The following procedure was used for synthesising the polymer: 0.29 g of ZnSO₄ and 0.34 g of morin were weighed in a glass tube and dissolved in 15 mL of methanol. Four millimoles of VP, 20 mmol of EDMA and 50 mg of AIBN were added into the solution. The oxygen was removed from the solution by bubbling of nitrogen through it for 10 min, then frozen with liquid nitrogen and sealed under vacuum. The polymerisation reaction was performed in a water bath at 75°C for 11 h. The synthesised polymer was ground in a mortar, dried and sieved to get particles with diameters in the range of 55–75 μm. Fine particles were removed by suspending polymer beads in methanol and decantation of methanol for three times. To remove templates, the remaining particles were treated with 2 M of HCl for 72 h, and the excess amount of HCl was washed by methanol. For confidence in complete removal of template from polymer, the concentration of Zn ions in aqueous phases after desired treatment periods were measured by ICP-OES. Finally, the particles were dried at 80°C. Figure 1 schematically shows the synthesis of molecular imprinted polymer. In the same way, the non-imprinted polymer (NIP) was also prepared without Zn–morin complex.

2.4 Complex adsorption–desorption studies

Adsorption of complex from aqueous solutions was investigated in batch experiments. The polymer beads were suspended in aqueous solutions and the pH was adjusted at 4 by dropwise addition 1 M of sodium hydroxide or HCl solutions. In adsorption step, 0.02 g of imprinted polymer particles was added into a 25 mL aqueous solution containing 25 μg of Zn and 50 μg of morin. The concentrations of Zn ion in aqueous phases after desired treatment periods were measured by ICP-OES. The instrument response was periodically checked with known Zn standard solutions. Three replicate extractions

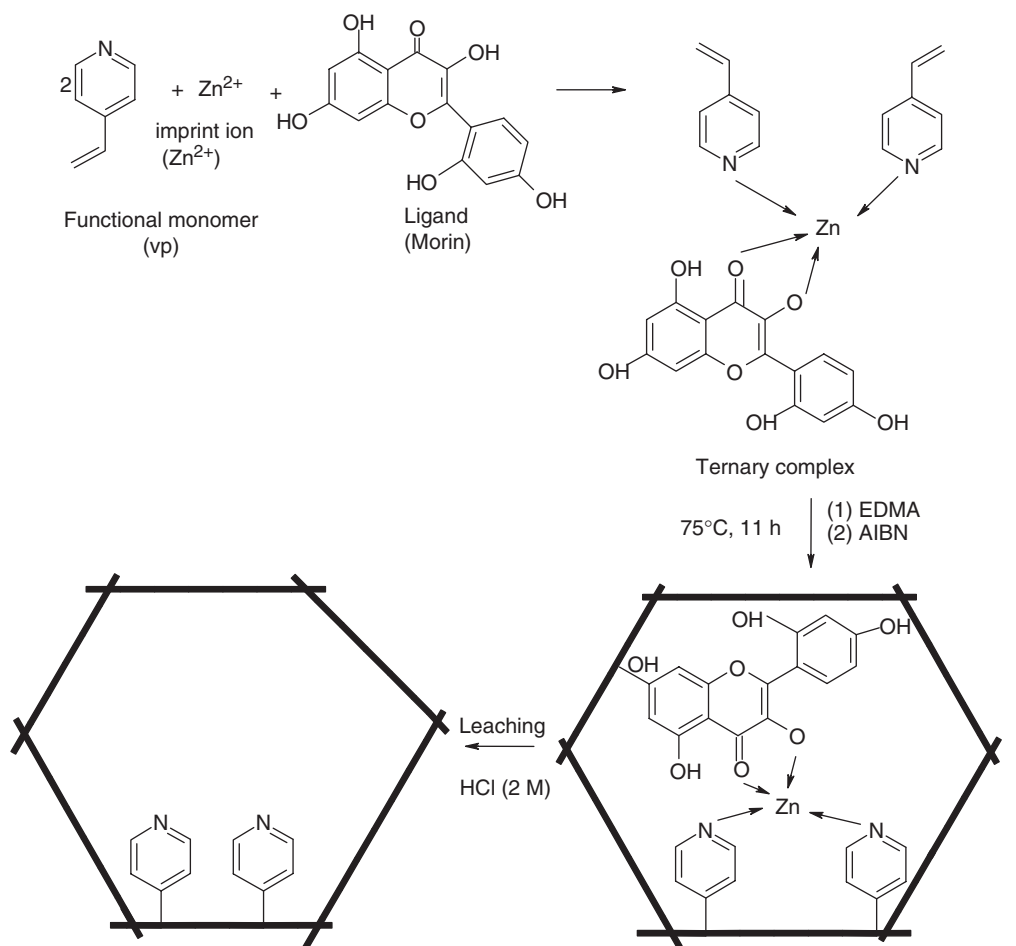


Figure 1. Preparation of ion-imprinted polymer material.

and measurements were performed for each aqueous solution. Percent extraction Zn of was calculated from this equation:

$$\% \text{ Extraction} = \left(\frac{C_0 - C_f}{C_0} \right) \times 100 \quad (1)$$

where C_0 and C_f are the concentrations of Zn ion before and after extraction in the solution.

The phase distribution ratio (D) was calculated using the following equation:

$$D = \left(\frac{C_0 - C_f}{C_f} \right) \left(\frac{V}{W} \right) \quad (2)$$

where W is the weight of the polymer in gram and V is the volume of the aqueous phase in millilitre.

The adsorbed Zn complex was desorbed from the MIP by putting washed polymer particles into a 10 mL of CH₂Cl₂-dimethyl sulfoxide (DMSO) (1:1, v/v).

The imprinted polymer containing Zn was placed in the desorption medium and stirred continuously at 600 rpm and room temperature for 40 min. Then, we added 10 mL of HNO₃ (0.5 M) to organic solvents and the concentration of Zn in liquid solution was measured to estimate the amount of Zn desorbed. The final Zn concentration in the aqueous phase was determined by ICP-OES. The unbound Zn amount to the polymer was obtained by subtracting the Zn bound amount to the polymer from that of the initial Zn loaded to the polymer.

3. Results and discussion

3.1 IR spectra

The IR spectra of NIP, unleached and leached Zn-imprinted polymer materials were recorded by using KBr pellet method (Figure 2). As is obvious, no absorption band is present in the region of 1648–1638 cm⁻¹, indicating the absence of vinyl groups in polymer materials. This confirms the complete polymerisation of vinyl pyridine. Meanwhile, there is other distinct difference between the IR spectra of the leached and unleached polymer. There is a broad band around 1565 cm⁻¹, which is assigned to ν (C=N) stretching vibration of pyridyl nitrogen in leached polymer. This band is lost in unleached polymer. But it was shifted to lower wavenumber on complexation with Zn ion in unleached polymer. A weak band of the aromatic ring near 1248 cm⁻¹ ν (C–N) present in the unleached polymer was also shifted to about 1258 cm⁻¹ in the leached polymer indicating the involvement of C=N group in VP while interacting with Zn ions. Further, the Zn²⁺ stretching mode at 722 cm⁻¹ disappeared in the leached and NIP particles.

3.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) curves may also be used to evaluate polymer purities. This is possible because the temperature range over which a mixture of compounds melts is dependent on their relative amounts. Figure 3 shows the DSC plots of unleached and leached Zn-imprinted polymer particles. In case of unleached Zn-imprinted polymer particles, the change in DSC plots at 80°C is due to the Zn–morin complex.

3.3 Effect of pH

The acidity of a solution has two effects on metal adsorption. First, protons in an acidic solution can protonate the binding sites of the chelating molecules. Secondly, the hydroxide in a basic solution may complex and precipitate many metals. A set of solutions containing 25 μ g of Zn and 50 μ g of morin in 25 mL were taken. The effect of pH on the adsorption of Zn ions from water samples was studied in the pH range of 2–6 for MIP and NIP. The pH of the solution was adjusted to the required value by adding 1 M sodium hydroxide and 1 M HCl. The effect of adsorption pH on the percent extraction of Zn is shown in Figure 4. The percentage of Zn adsorption increased by increasing pH to 4, and then decreased by further increasing pH, which agrees with the literature [11,12]. On one hand, at low pH, Zn–morin complex is not stable; and the competitive adsorption of hydrogen ions with Zn ions for morin groups at lower pH values account for

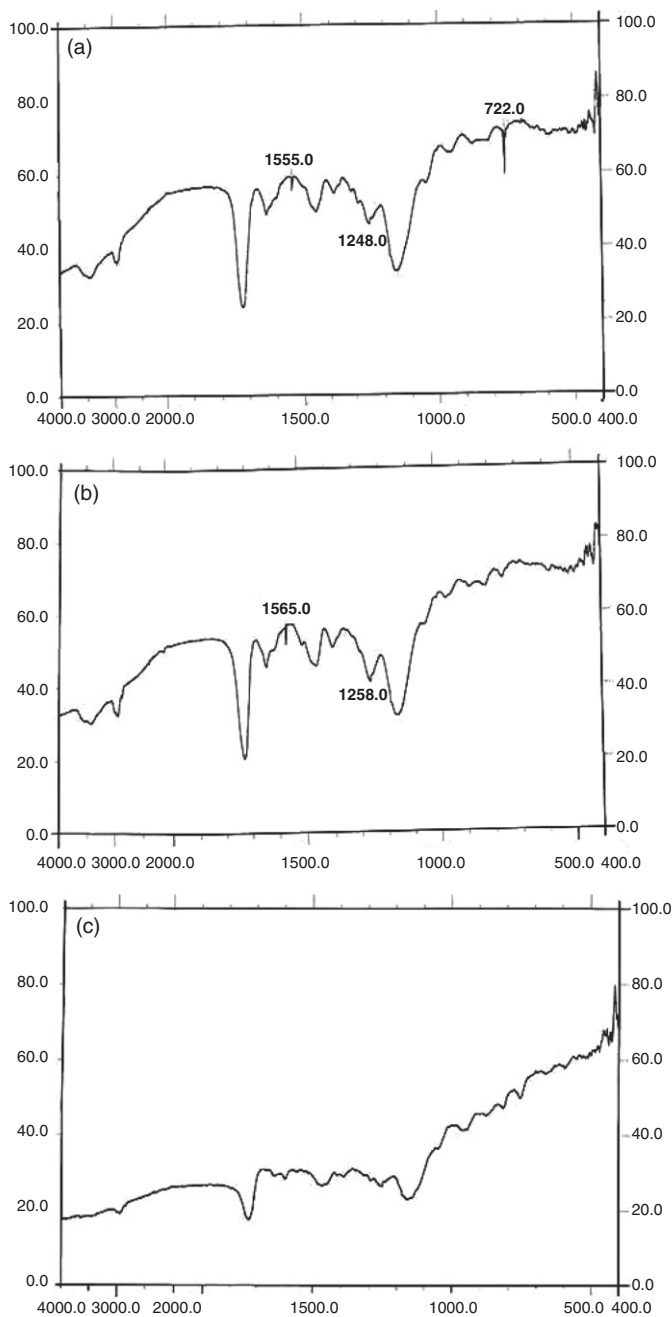


Figure 2. IR spectra of (a) unleached, (b) leached and (c) NIP.

the observed low efficiency and at high pH, Zn ion probably precipitates. On the other hand, this behaviour can be attributed to the molecular interactions between functional groups of polymer matrix and analyte. Hence, the pH was adjusted to 4 in all subsequent studies.

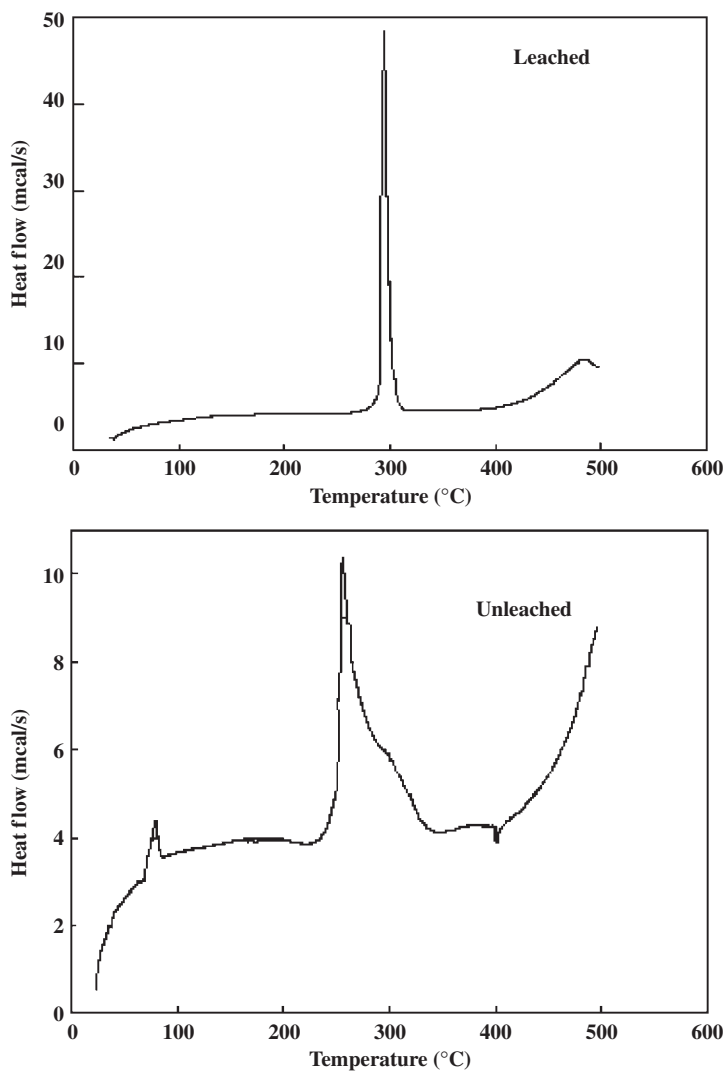


Figure 3. DSC plots of unleached and leached Zn-imprinted polymer materials.

3.4 Effect of amount of ligand

In order to investigate the optimum amount of morin on the quantitative extraction of Zn by the MIP, ion extraction was conducted by varying the [ligand]/[Zn] mole ratio from 1 to 6 and the results are shown in Figure 5. The extraction of Zn was found to be quantitative using [ligand]/[Zn] mole ratios greater than 2, due to the availability of more number of interaction accessible sites of morin. In the low amounts of ligand, may not create complex all the Zn ions. In order to create conditions that all Zn ions produce complex, extra amounts of ligand was added to the solution. Hence, subsequent extraction experiments were carried out with [ligand]/[Zn] ratio of 4.

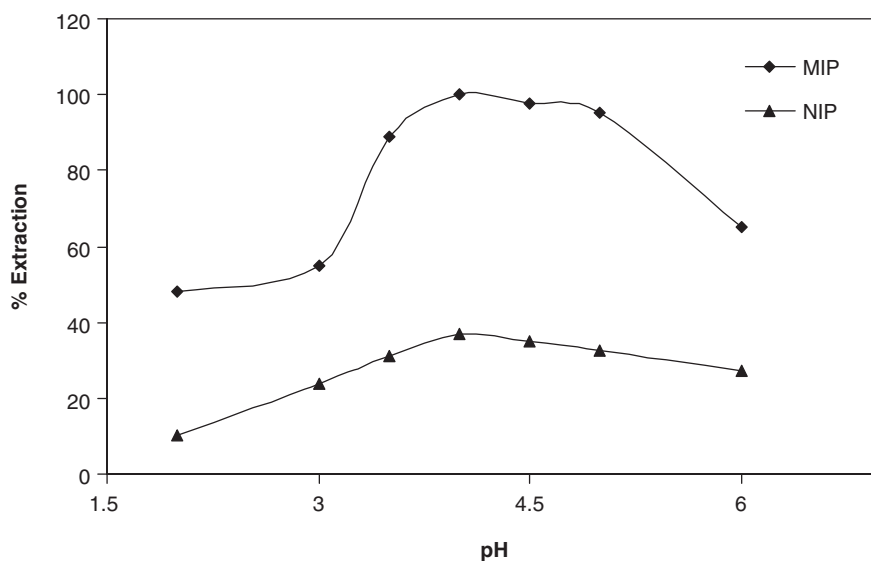


Figure 4. Effect pH on extraction efficiency of Zn ions.

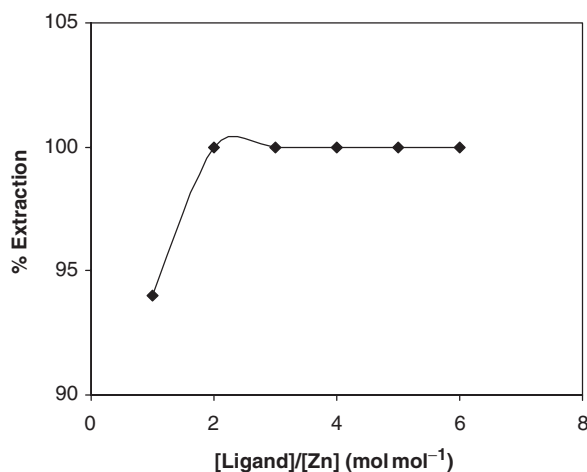


Figure 5. Effects of the amount of ligand on the extraction efficiency.

3.5 Choice of eluent

In order to choose a proper eluent for the retained Zn complex, after its extraction from water, the complex was stripped with different acidic solutions and organic solvents. From the data given in Table 2, it is obvious that 10 mL of a 1:1 (v/v) mixture of CH₂Cl₂–DMSO can accomplish the quantitative elution of complex from the imprinted polymer.

3.6 Effect of adsorption and desorption time

Table 3 shows, influence of adsorption and desorption time, on the percent of Zn ion using MIP and NIP particles. As can be seen from Table 3, a minimum of 60 min of

Table 2. Effect of type and amount of eluent on extraction efficiency.

Eluent	Volume (mL)	Recovery (%)
HCl 0.5 M	10.0	9.0
HCl 2 M	10.0	20.2
HCl 4 M	10.0	33.8
CH ₃ OH	10.0	10.0
CH ₃ OH-CH ₃ COOH (1:2)	15.0	65.0
CH ₃ OH-CH ₃ COOH (2:1)	15.0	45.0
DMSO-CH ₂ Cl ₂ (1:1)	100	100.0

Table 3. Influence of adsorption and desorption times on the percent extraction of Zn ion using MIP and NIP particles.

No.	Parameter	Extraction (%)	
		MIP	NIP
1	Adsorption time (min)		
	10	20	8
	20	79	12.5
	40	92	18.2
	60	100	20.7
2	Desorption time (min)		
	10	84	30.0
	20	95	42.3
	40	100	50.6
	60	100	55.0
	90	100	59.1

stirring is necessary to quantitative extraction of Zn present in 25 mL of solution for MIP. On the other hand, quantitative elution of adsorbed complex on MIP was occurred out after 40 min using 10 mL of a CH₂Cl₂-DMSO (1:1, v/v) of mixture. To make sure that adsorption and desorption Zn ions were complete occurred, the adsorption and desorption times were selected 80 and 60 min, respectively in subsequent studies.

3.7 Analytical performance

The breakthrough volume of sample solution was tested by dissolving 25 µg of Zn and 100 µg of ligand in 25, 50, 100, 250 and 500 mL solutions and proposed procedure was followed. The Zn ion recoveries for above volumes were 100, 100, 100, 95 and 88%, respectively. Thus, 250 mL was the maximum sample volume in which quantitative extraction of Zn is possible. At higher sample volumes the recovery decreased.

Under the optimum conditions above-mentioned, the calibration curve was linear over a concentration range of 25–200 $\mu\text{g L}^{-1}$. The least square equation at above dynamic linear range was as follows:

$$A = 1.7165 \times C(\mu\text{g L}^{-1}) - 0.0851 \quad (r^2 = 0.994) \quad (3)$$

The limit of detection (LOD) of the proposed methodology for the determination of Zn was studied under the optimal experimental conditions. The LOD obtained from $C_{\text{LOD}} = 3 S_d(\text{blank}) \text{ m}^{-1}$ was 2.9 $\mu\text{g L}^{-1}$.

All the statistical calculations are based on the average of triplicate extraction and measurement of each standard solution in the given range. The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 30.1. Table 4 compares the characteristic data of the present method with those reported in literature.

The determination of Zn ion was quantitatively in the presence of large amounts of alkaline and alkaline-earth ions and some transition metal ions, which indicates method suitability for natural water analysis (Table 5). In order to investigate the selective separation and determination of Zn ion from its ternary mixtures, an aliquot of aqueous solution (25 mL) containing 25 μg Zn and milligram amounts of Fe^{3+} , Cr^{3+} and Pb^{2+} were taken and the proposed procedure was followed. The results show that the recovery of Zn ion on MIP particles was only decreased 5%. Since the chloride,

Table 4. Comparison of the published methods with the proposed method in this work.

Method	Detection method	Detection limit ($\mu\text{g L}^{-1}$)	Reference
Cloud point extraction	Spectrofluorimetric	1.2	[13]
Sensor	Spectrophotometry	10.5	[14]
LLE	Fluorescence	7.0	[15]
SPE	ICP-OES	6.5	[16]
MIP	ICP-OES	2.9	This work

Table 5. Extraction of Zn from binary mixtures^a.

Foreign ion	Amount taken (mg) ^b	Recovery (%)
Li^+	12.5	100.0
Na^+	12.5	100.0
K^+	12.5	100.0
Mg^{2+}	12.5	100.0
Ca^{2+}	12.5	100.0
Sr^{2+}	12.5	100.0
Ba^{2+}	12.5	100.0
Cu^{2+}	2.5	95.0
Ni^{2+}	2.5	96.0
Cd^{2+}	2.5	95.5

Notes: ^aAmount of Zn taken is 25.0 μg .

^bA 12.5 mg is the maximum of cation that was tested.

nitrate and sulphate salts were employed in this study without any interference, their respective anions pose no possibility of interference.

Selecting coefficients of Zn ions over the other selected inorganic cations that coexisted with Zn ions in natural sources were studied by batch procedure. The MIP particles were tested for separation of Zn ions from Cd^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} ions either individually or in mixtures. The concentrations of transition metals were determined by ICP-OES. The selectivity of the Zn ions *versus* another cation was determined by the ratio of the two partition coefficients, D_{Zn}^{2+} and D_{m}^{n+} which is referred to the selectivity factor, α :

$$\alpha = \frac{D_{\text{Zn}}^{2+}}{D_{\text{m}}^{n+}} \quad (4)$$

The obtained results are summarised in Table 6. As it is clear from the results, quantitative separation of Zn from other cations is possible. Compared to other metal ions, the selectivity factor values demonstrate that the MIP synthesised for the Zn^{2+} has a higher selectivity for this ion due to match the charge, coordination number, coordination geometry and size of cavity of Zn^{2+} -imprinted polymer.

In order to assess the applicability of the method to real samples with different matrices, it was applied to the extraction and separation of Zn ions from 50 mL of three different samples taken from Chahnimeh reservoirs of Sistan Region, Iran and Zabol tap water. The reservoirs water samples were filtered through a 0.45 μm nylon membrane filter (Millipore, Bedford, MA, USA). Table 7 shows the extraction of 2.5 μg of added Zn ions from different samples. Results of three replicate analysis of each sample show that the Zn recovery was almost quantitative.

Table 6. Selectivity factors and distribution ratios of Zn-imprinted polymer particles.

Foreign ion	Distribution ratio (D)	Selectivity factor for MIP (α)	Selectivity factor for NIP (α)
Zn^{2+}	15	–	–
Cd^{2+}	0.87	17.2	5.6
Cu^{2+}	1.1	13.6	4.5
Ni^{2+}	1.4	10.7	3.9
Co^{2+}	1.2	12.5	4.1

Table 7. Recovery of 2.5 μg Zn added to 50 mL of samples.

Sample	Spiked amount ($\mu\text{g L}^{-1}$)	Zn found ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)
Tap water	–	–	–	–
Tap water	50.0	49.6	99.2	2.5
Chahnimeh water	–	–	–	–
Chahnimeh water	50.0	49.4	98.8	3.5
ZnSO_4 tablet	–	50.0	–	9.2
ZnSO_4 tablet	50.0	98.5	98.5	9.0

4. Conclusion

In the present study, a molecular imprinted polymer was prepared using the combination of VP as functional monomers, EDMA as cross-linker, and Zn–morin complex as template. The cross-linked imprinted adsorbents have good chemical and physical stability. The prepared MIP revealed high affinity and selectivity toward its template. The detection limit of $2.9 \mu\text{g L}^{-1}$ was greatly less than the maximum allowed limits of the EPA for Zn. The Zn-imprinted adsorbent, which was highly selective toward Zn ions, is expected to be a useful material for the interference-free extraction and preconcentration of Zn ions.

Zn(II) ion-imprinted particles enabled the selective extraction of Zn ions from a complex matrix, and after 10 times of absorption and desorption cycle, the recovery of adsorption capacity of Zn(II) on MIPs particles was only decreased 5%. The results suggested that these MIPs can be used several times without considerable loss of adsorption capacity.

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