Desalination and Water Treatment
www.deswater.com
22 (2010) 330–339
October
1944-3994 / 1944-3986 © 2010 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2010.1132

Synthesis and application of 5-amino-2-benzotriazol-2-yl-phenol for preconcentration and determination of zinc (II) in water samples by flame atomic absorption spectrometry

Homayon Ahmad Panahi[a]*, Mohammad Rabbani[b], Nader Zabarjad-Shiraz[a], Shirin Mofavvaz[b], Elham Moniri[c], Sahar Kanghari[a], Mahdieh Entezari[a], Azadeh Hasanzadeh[a]

[a]*Department of Chemistry, Islamic Azad University, Central Tehran Branch, Iran*
Tel. +98 (21) 44164539; Fax +98 (21) 88385778; email: h_ahmadpanahi@iauctb.ac.ir
[b]*Department of Sea Chemistry, Faculty of Marin of Sciences and Technology, Islamic Azad University, North Tehran Branch, Iran*
[c]*Department of Chemistry, Islamic Azad University, Varamin (Pishva) Branch, Iran*

Received 5 January 2009; Accepted in revised form 19 April 2010

ABSTRACT

A novel spherical 5-amino-2-benzotriazol-2-yl-phenol (ABP) chelating sorbent is synthesized simply and rapidly from 2-nitroanilin and 3-nitrophenol characterized (IR, ^{1}H NMR spectra and scanning electron microscopy) and studied for the preconcentration and determination of trace Zn(II) ion from aqueous solution samples. The concentration of metal ion in the solution was determined by flame atomic absorption spectrometry (FAAS). The optimum pH value for sorption of the metal ion was 6.5. The sorption capacity of ABP for Zn(II) was determined. The chelating ABP can be reused for 20 cycles of sorption-desorption without any significant change in sorption capacity. A recovery of 86% was obtained for the metal ion with 0.5 M HNO_3 as eluting agent. The equilibrium adsorption data of Zn(II) on sorbent were analyzed by the Langmuir and Freundlich models. Based on equilibrium adsorption data the Langmuir and Freundlich constants were determined 0.0074 and 1.200 at pH 6.5 and 25°C.

Keywords: Solid phase extraction; 5-amino-2-benzotriazol-2-yl-phenol; Zinc; Immobilization; Isotherm study

1. Introduction

Zinc is considered as an essential micronutrient for humans, plants and animals. It plays an important role in several biochemical processes [1]. Zinc(II) deficiency slows the growth and development of the neonate. Zinc(II) deficiency also leads to cognitive defects and impairs the immune system [2]. However, if it is in excess, it can also play an important role in the progression of several damages to human body, including disturbances in energy metabolism or increasing in oxidative stress [3]. Therefore, it is of great importance and significance for the environment science and life science to separate and determine trace zinc(II) in water samples. Although very sensitive analytical techniques such as FAAS [4,5], ICP-MS [6] and ICP-AES [7] are used for the determination of trace zinc(II), it is impossible to directly determine the amount of zinc(II) in water samples owing to the low

* Corresponding author.

concentration of zinc(II). In order to achieve accurate and reliable results, a preconcentration step is necessary when the concentration of zinc(II) is too low to be directly determined. The procedures for separation and preconcentration of zinc(II) had been reported extensively [4–15]. Various preconcentration techniques including solvent extraction [16], coprecipitation [17–19], cloud point extraction [20,21], ion-exchange [22] and electroanalytical techniques [23] have been used for the enrichment and separation of heavy metals at trace levels in various environmental samples including foods and natural waters by the researchers around the world. Solid phase extraction is an attractive separation–preconcentration technique for heavy metal ions with some important advantages: simplicity, flexibility, economic, rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents, more importantly environment friendly [24].

This paper proposes a novel method of preconcentration of trace zinc(II) in environmental water sample using 5-amino-2-benzotriazol-2-yl-phenol. 5-amino-2-benzotriazol-2-yl-phenol is an organic compound which is used in this research as chelating sorbent. This synthetic organic compound with having close N, O groups can chelate the metal ions like Zn(II). The purpose of the present study is to indicate the feasibility of using 5-amino-2-benzotriazol-2-yl-phenol as a solid-phase extractant for preconcentration of trace zinc(II) in environmental water samples. Trace zinc(II) can be retained on the surface of 5-amino-2-benzotriazol-2-yl-phenol and then desorbed with 0.5 M acid nitric prior to determination by FAAS. This proposed method has advantages of good accuracy, high recovery and preconcentration factor. It has been applied to the preconcentration and determination of trace zinc(II) in seawater.

2. Experimental

2.1. Instruments

A flame atomic absorption spectrometer of the GBC Awanta, 932 plus, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 $L.min^{-1}$, respectively) and inductive couple plasma (ICP), Varian, model Vista were used for measuring the concentration of metal ions. The pH measurements were made with Metrohm model 744 (Switzerland). IR spectra and NMR spectra were recorded on a FT-IR spectrometer Perkin Elmer Spectrum GX by KBr pellet method and Brucher 500, respectively. A pump (DV-42 N-250) was used control the flow of liquid through column. The sorption and desorption studies of metal on the chelating matrix were generally carried out on columns of 14 mm diameter and 7.8 cm in length.

2.2. Reagents and solutions

CH_3COOH, NaH_2PO_4, Na_2HPO_4, $ZnCl_2$, $SnCl_2$, HCl, H_2SO_4, HNO_3, NaNO2, NaOH, 2-nitro aniline, 3-nitro phenol, MeOH, Sn powder were products of Merck (Darmstadt, Germany).

All the solutions were prepared in deionized water using analytical grade reagents.

The stock solution (1000 $mg.L^{-1}$) of Zn(II), were prepared by dissolving appropriate amounts of $ZnCl_2$, in deionized water. 10 mL, 0.01 M acetic acid–acetate buffer (pH 3–6.5), 0.01 M phosphate buffer (pH 6.5–9) were used to adjust the pH of the solutions, wherever suitable.

3. Method

3.1. Synthesis of 5-amino-2-benzotriazol-2-yl-phenol (6) as chelating agent

Diazonium salt **2** was prepared by addition of (0.03 mol) $HCl/NaNO_2$ to (0.03 mol) 2-nitroanilin **1** at 0°C. This salt was stirred with solution of 0.03 mol 3-nitrophenol **3** in 30 mL water at pH 8 and produced azo compound **4**. Mixture of 5-nitro-2-((2-nitrophenyl)diazonyl)phenol **4** and 2 g zinc dust in 30 mL water, were added drop wise to a 25% w/w aqueous NaOH solution. The reaction mixture was stirred at 90°C for 1 h. The reaction mixture was acidified by concentrated HCl to pH 2–3 to remove unreacted zinc, and then filtered. The solid (5-nitro-2-benzotriazol-2-yl-phenol **5**) was recrystallized in methanol and then 0.01 mol of **5** treated with a reducing mixture of Sn powder (2.2 g) in 6 mL concentrated HCl. The mixture was stirred for 1.5 h at 80°C, gray precipitate filtered off and washed with water and recrystallized in methanol (5-amino-2-benzotriazol-2-yl-phenol **6**). The methodology used to synthesize 5-amino-2-benzotriazol-2-yl-phenol is summarized in Fig. 1. The ABP was grinded and sieved. The mesh size of used sorbent for adsorption of the metal ion was about 20.

3.2. Batch method

A sample solution (50 mL) containing (0.3 $\mu g.mL^{-1}$) of Zn(II) was taken in a glass stopper bottle, after adjusting its pH to the optimum value. The 0.05 g of 5-amino-2-benzotriazol-2-yl-phenol was added to the bottle and the mixture was shaken for optimum time. The ABP was filtered and sorbed metal ion was eluted with 0.5 M HNO_3 (10 mL). The concentration of metal ion in the elute was determined by FAAS.

3.3. Column method

5-amino-2-benzotriazol-2-yl-phenol (0.01 g) was packed in the polypropylene column (1.4×7.8 cm^2) and treated with 20 mL of 1 M HNO3 and washed with double-distilled water until the ABP was free from acid. 25 mL aliquot of the solution containing of Zn (II) in the concentration 0.6 $\mu g.mL^{-1}$ was passed through this column after adjusting its pH to an optimum value at flow

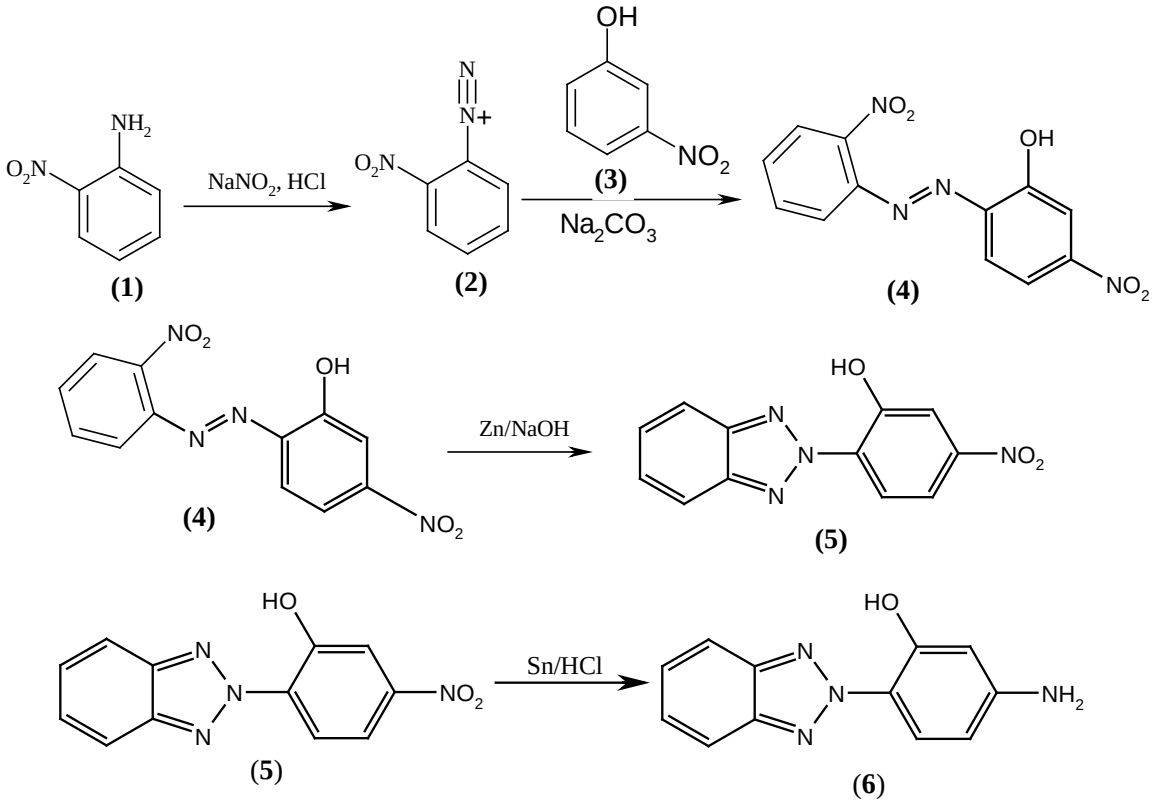

Fig. 1. The methodology of synthesize of 5-amino-2-benzotriazol-2-yl-phenol.

rate of 0.3–6.2 mL.min^{-1}. The stripping of the metal ions from the ABP column was carried out by 0.5 M HNO_3 (10 mL). The eluate was collected in 10 mL capacity volumetric flask. The collected solution was aspirated into the flame for atomic absorption spectrometer standardized prior to determination.

3.4. Isotherm studies

Isotherm studies were carried out by adding a fixed amount of adsorbent (0.02 g) to a series of beakers filled with 50 ml diluted solutions of Zn(II) (10–100 μg. mL^{-1}). The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (4 h) at 25, 35 and 45°C and optimum pH (6.5). pH adjustments have been done using 0.01 M acetate buffer. The beakers were then removed from the shaker, and the final concentration of Zn(II) in the solution was measured by FAAS. The amount of Zn(II) at equilibrium qe (mg/g) on 5-amino-2-benzotriazol-2-yl-phenol was calculated from the following equation:

$$q_e = (c_0 - c_e)V/W \quad (1)$$

where c_0 and c_e (mg/L) are the liquid phase concentrations of Zn(II) at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used.

In this paper the qe is amount of metal adsorbed per unit weight of the sorbent (mg. g^{-1}), K_L is the adsorption equilibrium constant, which is relate to the energy of adsorption (L.mg^{-1}), R_L dimensionless separation factor, R^2 correlation coefficient, n Freundlich isotherm constant related to adsorption intensity and recovery (%) is the percentage of the metal ion achieved by the sorbent.

4. Results and discussion

4.1. Characterization of ABP

Structure of compound **6** was elucidated by IR and ^{1}H NMR spectra.

5-nitro-2-((2-nitrophenyl)diazonyl)phenol (**4**). Dark red powder (73%), *mp* = 92°C.

IR (NaCl, cm^{-1}) 3479 (OH), 1617 (C=C), 1600 (N=N), 1530 and 1338 (NO_2).

5-nitro-2-benzotriazol-2-yl-phenol (**5**). Light brown powder (84%), *mp* = 210°C.

IR (NaCl, cm^{-1}) 3257 (OH), 1650 (C=C), 1606 (N=N) 1555 and 1350 (NO_2).

5-amino-2-benzotriazol-2-yl-phenol (**6**). Gray powder (81%), *mp* = 280°C.

IR (NaCl, cm^{-1}), 3378 (OH), 3310 and 3224 (NH_2), 1601 (C=C), 1569 (C=C aromatic), 1515 (C=N) (see Fig. 2).

^{1}H NMR (see Fig. 3) (500.1 MHz, $CDCl_3$, D_2O)δ :9.24 (1

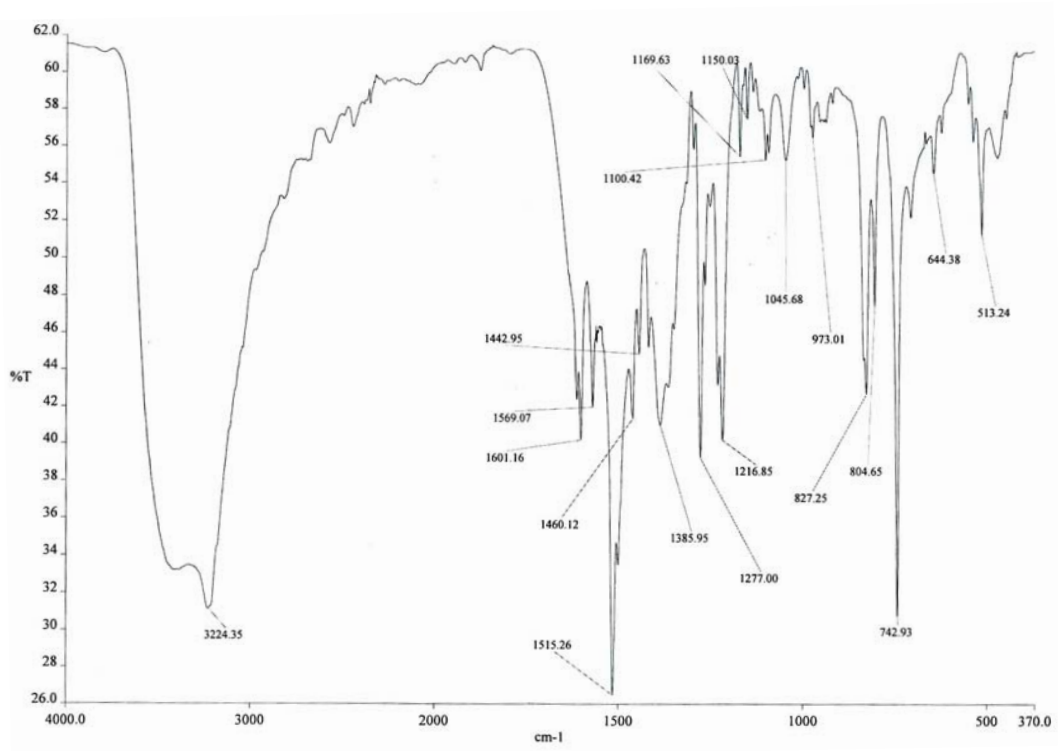

Fig. 2. IR spectrum of 5-amino-2-benzotriazol-2-yl-phenol.

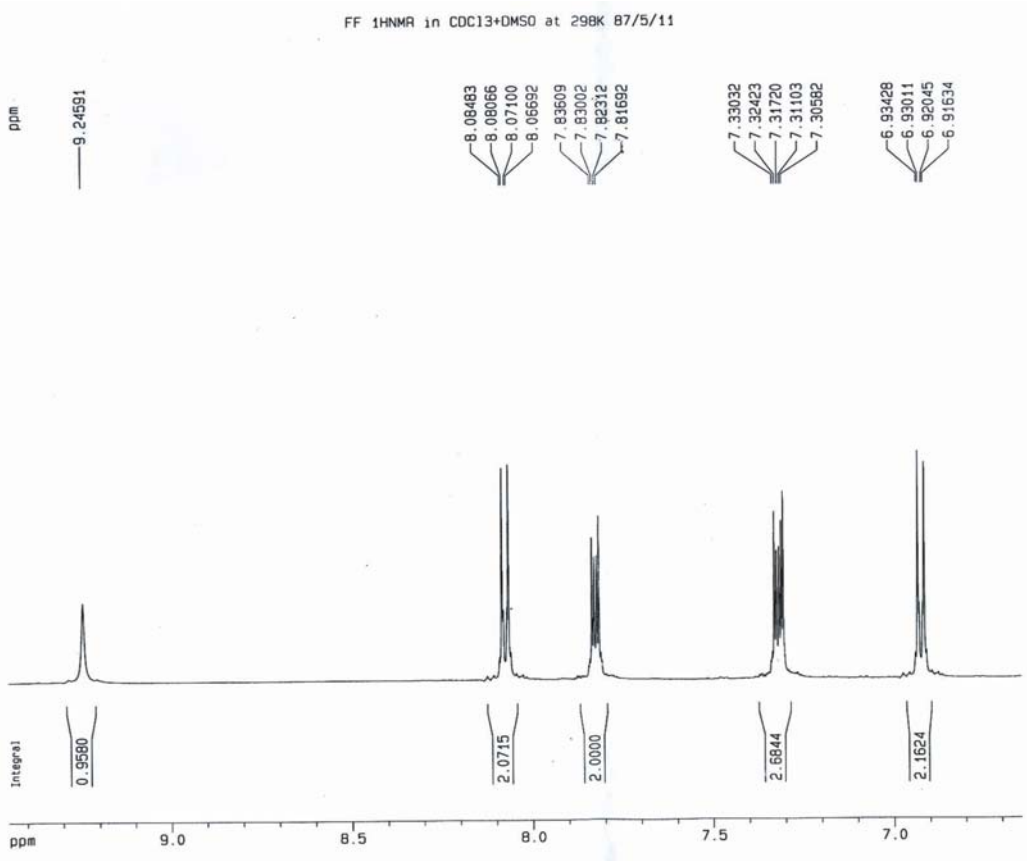

Fig. 3. Expanded 1H-NMR spectrum of 5-amino-2-benzotriazol-2-yl-phenol.

H, s, OH hydrogen bonding), 8.07 (2H, d, $^3J_{HH}$ = 9.0 Hz, 2 CH), 7.83 (H, d, $^3J_{HH}$ = 6.5 Hz, CH), 7.82 (1 H, d, $^3J_{HH}$ = 6.5 Hz, CH), 7.30–7.33 (3H, m, CH and NH_2), 6.92 (2H, d, $^3J_{HH}$ = 9 Hz, 2 CH).

4.2. Scanning electron microscopy

The surface morphology and external structure of ABP was investigated by the scanning electron micrographs which are given in Fig. 4. The surface of ABP has a smooth and highly homogeneous appearance. As clearly seen here, the surface of the synthesized ABP has a rod shape. The diameters of the rods on an average are 190 nm. The size of the large pores between the clusters in Fig. 4 is about 10 μm. It is these macropores that would reduce diffusional mass transfer resistance and facilitate convective mass transport because of their spacious internal surface area.

4.3. Metal sorption as a function of pH

The degree of metal sorption at different pH values was determined by batch equilibration technique. A set of solutions (volume of each 50 mL) containing 0.3 μg.mL^{-1} of Zn(II) was taken. Their pH values were adjusted in range 3–9 with 0.01M acetate and/or phosphate buffer solutions. The 0.05 g of 5-amino-2-benzotriazol-2-yl-phenol was added to each solution and the mixture was shaken for 4 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring Zn(II) content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the metal ion from sorbent with 0.5 M nitric acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Fig. 5. The maximum recovery was 86% at pH 6.5.

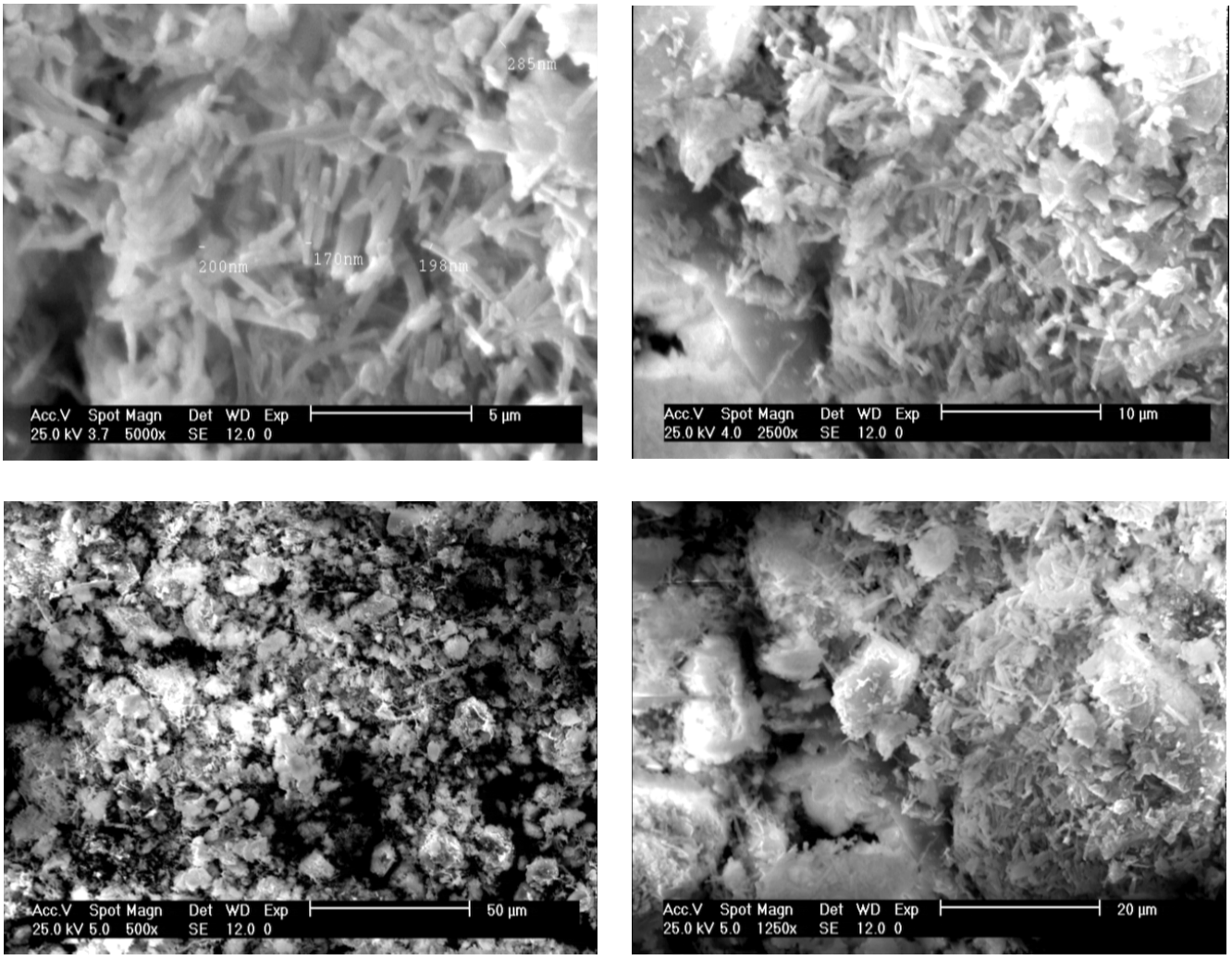

Fig. 4. SEM photograph of 5-amino-2-benzotriazol-2-yl-phenol.

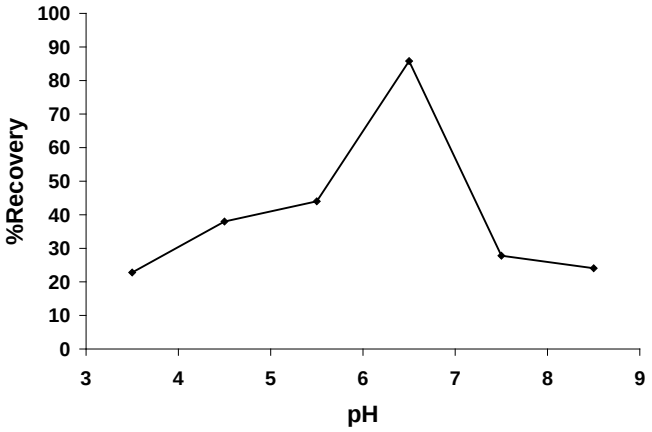

Fig. 5. Effect of pH sorption of Zn(II) onto 5-amino-2-benzotriazol -2-yl-phenol.

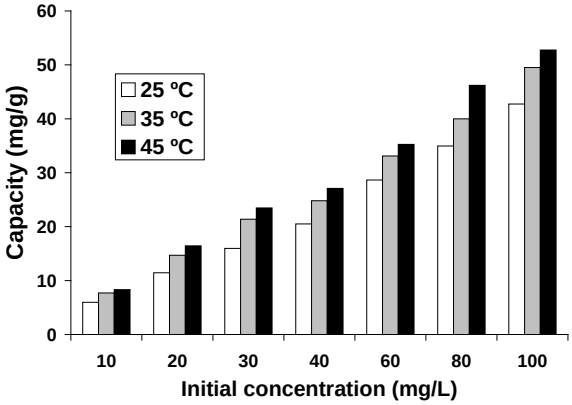

Fig. 6. Effect of initial concentration of the Zn in the solution and temperature on capacity sorption of Zn(II) onto 5-amino-2-benzotriazol-2-yl-phenol.

4.4. Total sorption capacity

0.02 g of sorbent was stirred for 5 h with 50 mL solution containing 10–100 μg.mL^{-1} of Zn(II), at optimum pH and different temperature. The metal ion concentration in the supernatant liquid was estimated by FAAS. The sorption capacity of the ABP for the metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption. The saturated adsorption capacity of the ABP is shown in Fig. 6. This figure indicates the effect of initial concentration of the Zn(II) in the solution and temperature on capacity sorption of Zn(II) by 5-amino-2-benzotriazol-2-yl-phenol. The capacity goes up with temperature increasing and initial concentration of the Zn in the solution.

4.5. Stability and reusability of the ABP

Zn(II) was sorbed and desorbed on 1 g of the ABP several times. It was found that sorption capacity of ABP after 20 cycles of its equilibration with Zn(II), changes less than 5%. Therefore, repeated use of the ABP is feasible. The ABP after loading it with samples can be readily regenerated with 0.5 M HNO_3. The sorption capacity of the ABP stored for more than 6 month under ambient conditions has been found to be practically unchanged.

4.6. Effect of flow rate

The metal ion sorption on 5-amino-2-benzotriazol-2-yl-phenol (0.01 g) packed column studied at various flow rates of Zn(II) solutions. The optimum flow rate for loading Zn(II) on to ABP was found to be 0.4 mL.min^{-1}. A flow rate < 0.4 mL.min^{-1} was not employed to avoid the longer time of analysis. It was observed that more than 80% sorption of Zn(II) on the ABP occurred at flow rate < 0.5 mL.min^{-1} (Fig. 7). The decrease in the percentage of sorption at the upper flow rate is probably because the metal ion does not equilibrate sufficiently with the matrix. For stripping off the bounded Zn(II) on the 5-amino-2-benzotriazol-2-yl-phenol, 0.5 M nitric acid was applied.

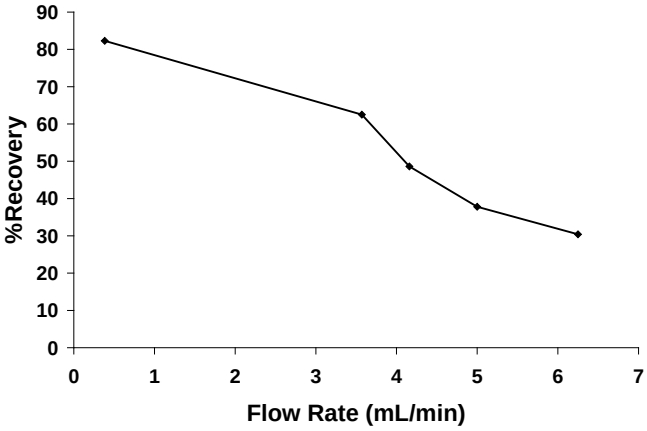

Fig. 7. Effect of flow rate on sorption of Zn(II) on 5-amino-2-benzotriazol -2-yl-phenol.

4.7. Effect of temperature

The adsorption studies were carried out at three different temperatures 25, 35 and 45°C, and the results of these experiments are shown in Fig. 8. The adsorption capacity increases with temperature increasing, indicating that the adsorption is an endothermic process (Table 1). This may be a result of increase in the mobility of Zn(II) with temperature increasing [25]. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Table 1 also shows that maximum adsorption capacities of 5-amino-2-benzotriazol-2-yl-phenol were determined as 0.98, 1.04 and 1.23 mg/g at 25, 35 and 45°C, respectively.

Table 1
Langmuir, Frendlich isotherm and separation factors (R_L) for adsorption of Zn(II)

Temperature (°C)	Langmuir isotherm model				Frendlich isotherm model		
	q_{max} (mg/g)	K_L (L/mg)	R^2	R_L	K_F (mg/g) (L/mg)$^{1/n}$	n	R^2
25	106.7	0.0074	0.9776	0.580	1.200	1.230	0.9979
35	91.0	0.0132	0.9554	0.431	2.056	1.376	0.9895
45	97.1	0.0142	0.9538	0.413	2.357	1.387	0.9859

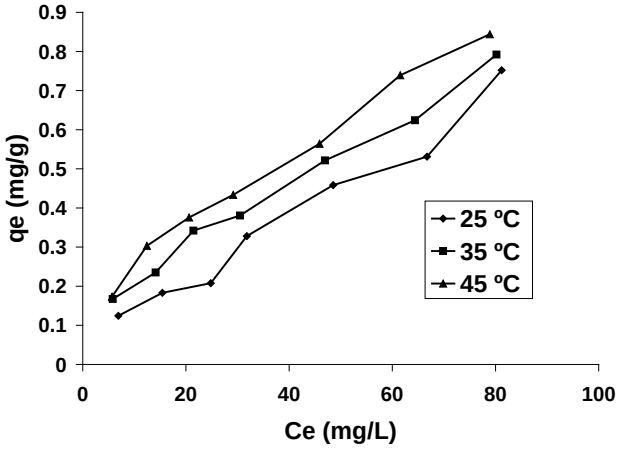

Fig. 8. Adsorption isotherms for Zn(II) on 5-amino-2-benzotriazol-2-yl-phenol at different temperatures.

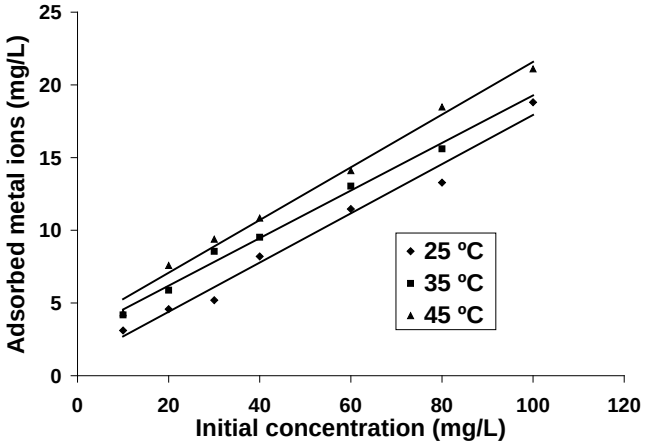

Fig. 9. Effect of concentration for the uptake of Zn(II) on 5-amino-2-benzotriazol-2-yl-phenol at different temperatures.

The adsorption of Zn(II) was also recorded in the concentration range from 10–100 mg.L^{-1}, at optimum pH and temperatures 25, 35 and 45°C (Fig. 9). Fig. 9 indicates that the adsorption of Zn(II) by 5-amino-2-benzotriazol-2-yl-phenol increases with the increase in temperature, indicating thereby the process to be endothermic in nature.

4.8. Adsorption isotherms

The Langmuir equation is given as follows [26]:

$$q_e = q_{max} K_L c_e / (1 + K_L c_e) \quad (2)$$

where q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g) and K_L is the Langmuir constant (L/mg). Eq. (2) can be rearranged to a linear form:

$$c_e / q_e = (1/q_{max} K_L) + (c_e / q_{max}) \quad (3)$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of c_e/q_e vs. c_e (Fig. 10).

Conformation of the experimental data in to the Langmuir isotherm model indicates the homogeneous nature of 5-amino-2-benzotriazol-2-yl-phenol surface. Langmuir parameters calculated from Eq. (3) are listed in Table 1.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor, R_L, defined as [27]:

$$R_L = 1/(1 + K_L c_0) \quad (4)$$

Table 1 shows that the values of R_L (0.41–0.58) were in the range of 0–1 at optimum pH which confirms the favorable uptake Zn(II) (Table 2).

The Freundlich equation is an empirical equation employed to the described heterogeneous systems, in which it is characterized by the heterogeneity factor 1/n. Hence, the empirical equation can be written [28]:

$$q_e = K_F c_e^{1/n} \quad (5)$$

where K_F is the Freundlich constant (mg/g) (L/mg)$^{1/n}$ and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (5):

$$\ln q_e = \ln K_F + 1/n \ln c_e \quad (6)$$

Therefore, a plot of ln q_e vs. ln c_e (Fig. 11) enables the constant K_F and exponent 1/n to be determined. The Freundlich equation predicts that Zn(II) concentration on the adsorbent will increase so long as there is an increased in Zn(II) concentration in the liquid.

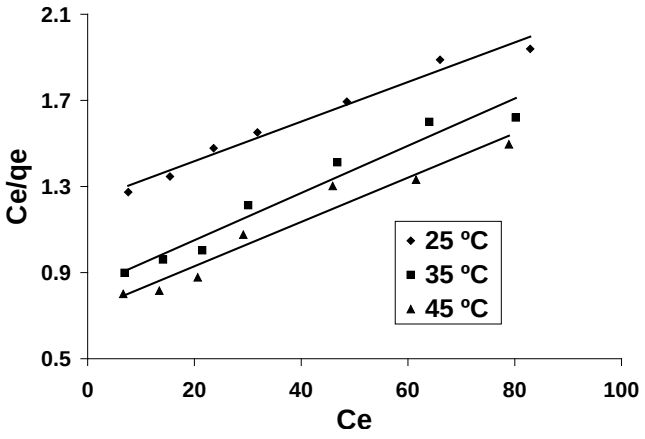

Fig. 10. Langmuir isotherm for Zn(II) adsorption onto 5-amino-2-benzotriazol-2-yl-phenol at different temperatures.

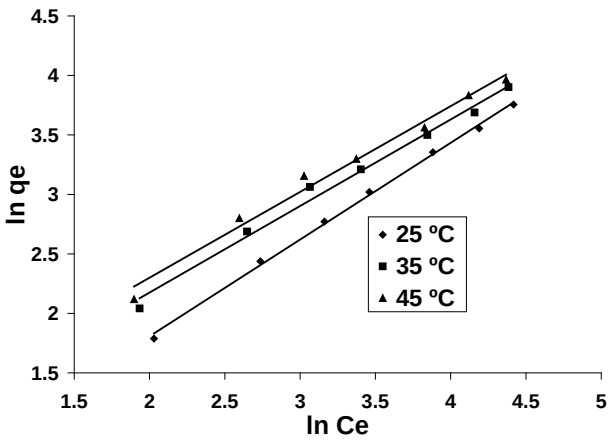

Fig. 11. Freundlich isotherm for Zn(II) adsorption onto 5-amino-2-benzotriazol-2-yl-phenol at different temperatures.

Table 2
The parameter R_L indicated the shape of isotherm

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 3
Effect of other ions on sorption

Interfering ions	Adsorbed Pb(II) ($mg.L^{-1}$)	Adsorption loss (%)
—	4.08	0
Co(II)	3.96	2.9
Ni(II)	3.98	2.5
Ba(II)	4.07	0
Hg(II)	3.95	3
Ag(I)	3.79	7.1
Fe(II)	3.68	9.8
Mg(II)	4.07	0
Cu(II)	4.04	1
Ca(II)	4.02	1

4.9. Comparison with other methods

Comparative information from some studies on preconcentration of Zn(II) by various methods for the figure of merits is given in Table 5. The sorption capacity of the present sorbent is superior in comparison to all the matrices shown in Table 4. This new developed method has been successfully applied to the analysis of trace metal ions in natural water sample.

Table 4
Results obtained for metal determination in water sample

Analyte	Zn(II)
Before preconcentration, ppb	0.915
After preconcentration, ppb	69
Preconcentration factor	100
Recovery, %	75.4
Standard deviation	0.070
Relative standard deviation[a], %	4.2

[a] For three determinations

4.10. Effect of foreign ions

In order to evaluate the selectivity of the preconcentration system, the effect of some metal ions (10 $mg.L^{-1}$) on the sorption behavior of Zn(II) ion (concentration 10 $mg.L^{-1}$) was investigated. The result is shown in Table 3. This table indictes that the most effective ions on adsorption of Zn(II) on 5-amino-2-benzotriazol-2-yl-phenol are Ag(I) and Fe(II). The effects of other mentioned foreign ions at given concentrations are negligible. The adsorption of Zn(II) on the 5-amino-2-benzotriazol-2-yl-phenol in the presence of all mentioned ions (concentration of each metal ions 10 mg. L^{-1}) shows that Zn(II) can be determined quantitatively in the environmental samples.

4.11. Application of the method

5-amino-2-benzotriazol-2-yl-phenol was used to preconcentrate and determine Zn(II) ions in the Persian Gulf (Nakhle Nakhoda, Iran). The pH of the water sample (acidified with 0.1 M HNO3) was adjusted to the optimum pH. Solid phase extraction with 5-amino-2-benzotriazol-2-yl-phenol coupled with ICP determination was supplied to determine Zn(II) in the water sample. The

Table 5
Comparison of capacities

Sorbent used	Capacity ($mg.g^{-1}$)	Ref.
Amberlite XAD-7/Xylenol orange	1.8	29
Amberlite XAD-2/ 2-aminoacetylthiophenol	19.54	30
Amberlite XAD-2 (AXAD-2-DHP)/2, 3-dihydroxypyridine	11.48	31
Silica gel/p-toluenesulfonylamide	12.6	32
Silica gel/o-dihydroxybenzene	10.98	33
Silica gel/4-(8-hydroxy-5-quinolylazo) naphthalenesulfonic acid	39.43	34
p-tert-butylcalix[4]arene-1,2-crown-4-anchored chloromethylated	9.34	35
p-tert-butylcalix[8]arene, XAD-4	47.16	36
o-vanilinthiosemicarbozone, XAD-2	0.14	37
Tiron, XAD-2 [23]	11.11	38
Ammonium pyyrolidine dithiocarbamate, XAD-4	10.59	39
Piperidine dithiocarbamate, XAD-4	10.26	39
o-aminobenzoic acid, XAD-4	7.9	40
1, 8-dihydroxyanthraquinone anchored on silica gel	11.76	9
5-amino-2-benzotriazol-2-yl-phenol (our sorbent)	47.05	

results are shown in Table 4. These results demonstrate the applicability of the procedure for Zn determination in the samples.

5. Conclusion

A new sorbent was synthesized with 2-nitroanilin and 3-nitrophenol. The synthesis of the sorbent is simple and economical. The solid phase extraction (SPE) procedure developed in this paper using 5-amino-2-benzotriazol-2-yl-phenol facilitates a 10-fold preconcentration of zinc(II) from dilute aqueous solutions. The sorbent has a good potential for enrichment of trace amount of Zn(II) from large sample volumes through batch binding and column SPE. The optimum flow rate for loading Zn(II) on to sorbent was found to be 0.4 $mL.min^{-1}$ in column method. Zn(II) adsorption was due to 5-amino-2-benzotriazol-2-yl-phenol–metal ion interactions. The sorbent also presents the advantage of high adsorption capacity, good reusability and high chemical stability. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 106.7, 91.0 and 97.1 (mg/g) at 25, 35, and 45°C, respectively. The RL values showed that 5-amino-2-benzotriazol-2-yl-phenol was favorable for the adsorption of Zn(II). Preconcentration by this ABP combined with FAAS and ICP-AES can be applied to the determination of trace zinc(II) ions in water and the mineral reference sample with satisfactory results.

References

[1] J.B. Neto, V. Stefan, B.B. Mendonca, W. Bloise and A.V.B. Castro, Single-sample cloud point determination of iron, cobalt and nickel by flow injection analysis flame atomic absorption spectrometry application to real samples and certified reference materials, Nutr. Res., 15 (1995) 335–358.

[2] B.N. Ames, DNA damage from micronutrient deficiencies is likely to be a major cause of cancer, Mutat. Res., 475 (2001) 7–20.

[3] J.Y. Koh, Zinc and disease of the brain, Mol. Neurobiol., 24 (2001) 99–106.

[4] K.A. Tony, S. Kartikeyan, B. Vijayalakshmy, T.P. Rao and C.S.P. Iyer, Flow injection on-line preconcentration and flame atomic absorption spectrometric determination of iron, cobalt, nickel, manganese and zinc in sea-water, Analyst, 124 (1999)R.J. Cassella, D.T. Bitencourt, A.G. Branco, S.L.C. Ferreira, D.S. Jesus, M.S. Carvalhod and R.E. Santelli, On-line preconcentration system for flame atomic absorption spectrometry using unloaded polyurethane foam: determination of zinc in waters and biological materials, J. Anal. At. Spectrom., 14 (1999) 1749.

[5] D. Kara, A. Fisher and S.J. Hill, Preconcentration and determination of trace elements with 2,6-diacetylpyridine functionalized Amberlite XAD-4 by flow injection and atomic spectroscopy, Analyst, 130 (2005) 1518.

[6] M. Zougagh, P.C. Rudner, A.G. Torres and J.M.C. Pavón, Application of Doehlert matrix and factorial designs in the optimization of experimental variables associated with the on-line preconcentration and determination of zinc by flow injection inductively coupled plasma atomic emission spectrometry, J. Anal. At. Spectrom., 15 (2000) 1589.

[7] V.A. Lemos,W.N.L. Santos, J.S. Santos and M.B. Carvalho, On-line preconcentration system using a minicolumn of polyurethane foam loaded with Me-BTABr for zinc determination by flame atomic absorption spectrometry, Anal. Chim. Acta, 481 (2003) 283–290.

[8] A. Goswami and A.K. Singh, 1,8-dihydroxyanthraquinone anchored on silica gel: synthesis and application as solid phase extractant for lead(II), zinc(II) and cadmium(II) prior to their determination by flame atomic absorption spectrometry, Talanta, 58 (2002) 669–678.

[9] M. Ulewicz, W. Walkowiak and R.A. Bartsch, Ion flotation of zinc(II) and cadmium(II) with proton-ionizable lariat ethers — Effect of cavity size, Separ. Purif. Technol., 48 (2006) 264–269.

[10] M. Kumar, D.P.S. Rathore and A.K. Singh, Amberlite XAD-2 functionalized with o-aminophenol: synthesis and applications as extractant for copper(II), cobalt(II), cadmium(II), nickel(II),

zinc(II) and lead(II), Talanta, 51 (2000) 1187–1196.
[11] P.K. Tewari and A.K. Singh, Thiosalicylic acid-immobilized Amberlite XAD-2: metal sorption behaviour and applications in estimation of metal ions by flame atomic absorption spectrometry, Analyst, 125 (2000) 2350.
[12] B.R. Reddy and D.N. Pridy, Process development for the separation of copper(II), nickel(II) and zinc(II) from sulphate solutions by solvent extraction using LIX 84 I. Separ. Purif. Technol., 45 (2005) 163–167.
[13] H. Bag, A.R. Turker, R. Coskun, M. Sacak and M. Yigitoglu, Determination of zinc, cadium, cobalt and nickel by flame atomic absorption spectrometry after preconcentration by poly ethylene terephthalate fibers grafted with methacrylic acid. Spectrochim. Acta B, 55 (2000) 1101–1108.
[14] Q.F. Hu, G.Y. Yang, J.H. Yang and J.Y. Yin, Study on determination of iron, cobalt, nickel, copper, zinc and manganese in drinking water by solid-phase extraction and RP-HPLC with 2-(2-quinolinylazo)-5-diethylaminophenol as precolumn derivatizing reagent. J. Environ. Monit., 4 (2002) 956–959.
[15] T.P. Rao, P. Metilda and J.M. Gladis, Overview of analytical methodologies for sea water analysis: Part I—Metals, Crit. Rev. Anal. Chem., 35 (2005) 247–288.
[16] L. Elci, M. Soylak and B. Ozcan, Coprecipitation of Cu(II), Ni(II), Fe(III), Cd(II), Pb(II), and Co(II) in wastewater, sediment, and metallic zinc samples with HMDTC-HMA for flame atomic absorption spectrometric determination, Anal. Lett., 36 (2003) 987–999.
[17] K. Prasad, P. Gopikrishna, R. Kala, T. Prasada Rao and G.R.K. Naidu, Solid phase extraction vis-a-vis coprecipitation preconcentration of cadmium and lead from soils onto 5,7-dibromoquinoline-8-ol embedded benzophenone and determination by FAAS, Talanta, 69 (2006) 938–945
[18] M.G.A. Korn, J.B. de Andrade, D.S. de Jesus, V.A. Lemos, M.L.S.F. Bandeira, W.N.L. dos Santos, M.A. Bezerra, F.A.C. Amorim, A.S. Souza and S.L.C. Ferreira, Separation and preconcentration procedures for the determination of lead using spectrometric techniques: A review, Talanta, 69 (2006) 16–24.
[19] A.M.A. Khadar and A. Varghese, Simultaneous determination of titanium and molybdenum in alloy steels using derivative spectrophotometry in neutral micellar medium, Indian J. Chem. Technol., 12 (2005) 701–707.
[20] D.L. Giokas, E.K. Paleologos, S.M. Tzouwara-Karayanni and M.I. Karayannis, Single-sample cloud point determination of iron, cobalt and nickel by flow injection analysis flame atomic absorption spectrometry — Application to real samples and certified reference materials, J. Anal. At. Spectrom., 16 (2001) 521–526.
[21] A. Smara, R. Delimi, C. Poinsignon and J. Sandeaux, Electroextraction of heavy metals from diluted solutions by a process combining ion-exchange resins and membranes, Separ. Purif. Technol., 44(3) (2005) 271–277.
[22] T.Z. Peng, Z. Tang, G.S. Wang and B.E. Shen, Differential pulse voltammetric determination of lead(II) with benzoin oxime-modified carbon paste electrodes, Electroanalysis, 6 (1994) 597–603.
[23] T.P. Rao, P. Metilda and J.M. Gladis, Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination — An overview, Talanta 68 (2006) 1047–1064.
[24] M. Alkan and M. Dogan, Adsorption kinetics of victoria blue onto perlite, Fresen. Environ. Bull., 12 (2003) 418.
[25] L. Langmuir, The adsorption of gases on plane surfaces of glass mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.
[26] K.L. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, Pore and solid-diffusion kinetics in fixed bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam., 5 (1966) 212–223.
[27] H.M.A. Frendlich, Concerning adsorption in solutions. Z. Phys. Chem. Stöchiometrie Verwandtschaftslehre, J. Phys. Chem., 57 (1906) 385–470.
[28] P.K. Tewari and A.K. Singh, Amberlite XAD-7 impregnated with Xylenol Orange:a chelating collector for preconcentration of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III) ions prior to their determination by flame AAS, Fresenius J. Anal. Chem., 367 (2000) 562–567.
[29] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng and J. Liu, Preconcentration and determination of trace elements with 2-aminoacetylthiophenol functionalized Amberlite XAD-2 by inductively coupled plasma–atomic emission spectrometry, Talanta, 62 (2004) 207–215.
[30] G. Venkatesh, A.K. Jain and A.K. Singh, 2,3-dihydroxypyridine loaded amberlite XAD-2 (AXAD-2-DHP): Preparation, sorption–desorption equilibria with metal ions, and applications in quantitative metal ion enrichment from water, milk and vitamin samples, Microchim. Acta, 149 (2005) 213–225.
[31] Q. He, X.J. Chang, X.P. Huang and Z. Hu, Metal ion enrichment with Amberlite XAD-2 functionalized with Tiron: analytical applications, Microchim. Acta, 160 (2008) 147–152.
[32] G. Venkatesh, A.K. Singh and B. Venkataramani, Silica gel loaded with o-dihydroxybenzene: Design, metal sorption equilibrium studies and application to metal enrichment prior to determination by flame atomic absorption spectrometry, Microchim. Acta, 144 (2004) 233–241.
[33] X. Chang , H. Luo, Y. Cui, X. Zhu, Y. Zhai, Z. Hu and Q. He, ICP-OES determination of trace metal ions after preconcentration by 4-(8-hydroxy-5- uinolylazo) naphthalene sulfonic acid modified silica gel, J. Mol. Struct, 891 (2008) 45–49.
[34] S. Seyhan , M. Colak, M. Merdivan and N. Demirel, Solid phase extractive preconcentration of trace metals using p-tert-butylcalix[4]arene-1,2-crown-4-anchored chloromethylated polymeric resin beads, Anal. Chim. Acta, 584 (2007) 462–468.
[35] R. Pathak and G.N. Rao, Synthesis and metal sorption studies of p-tert-butylcalix[8]arene chemically bound to polymeric support, Anal. Chim. Acta, 335 (1996) 283–290.
[36] V.K. Jain, S.S. Sait, P. Shrivastav and Y.K. Agrawal, Application of chelate forming resin Amberlite XAD-2-o-vanillinthiosemicarbazone to the separation and reconcentration of copper(II), zinc(II) and lead(II), Talanta, 45 (1997) 397–404.
[37] M. Kumar, D.P.S. Rathore and A.K. Singh, Metal ion enrichment with Amberlite XAD-2 functionalized with Tiron: analytical applications, Analyst, 125 (2000) 1221.
[38] A. Ramesh, K.R. Mohan and K. Seshaiah, Preconcentration of trace metals on Amberlite XAD-4 resincoated with dithiocarbamates and determination by inductively coupled plasma-atomic emission spectrometry in saline matrices, Talanta, 57 (2002) 243–252.
[39] S.D. Cekic, H. Filik and R. Apak, Use of an o-aminobenzoic acid-functionalized XAD-4 copolymer resin for the separation and preconcentration of heavy metal (II) ions, Anal. Chim. Acta, 505 (2004) 15–24.