



Study on solid-phase extraction and flame atomic absorption spectrometry for the selective determination of cadmium in water and plant samples with modified clinoptilolite

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ABSTRACT

A sensitive, simple separation and solid-phase procedure, which is sorption and desorption of cadmium on modified clinoptilolite zeolite (with surfactant and neothorine), for preconcentration of cadmium prior to analysis by FAAS is described. The sorbent has exhibited good sorption potential for cadmium at pH 5. Cadmium was eluted from the column by nitric acid which resulted in preconcentration factor of 160. Thermodynamic behaviors for the process are investigated and adsorption process is interpreted in term of Freundlich equation. A detection limit of 0.015 ng mL^{-1} was obtained and it is shown that calibration curve is linear from 0.01 to $4.0 \mu\text{g mL}^{-1}$ in the final solution. Furthermore, the effects of various parameters such as pH, flow rate of the sample and eluent solution were studied. This method was successfully applied for determination of cadmium in various plant and real water samples.

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1. Introduction

The levels of heavy metals circulating in the environment have seriously increased during the last few decades due to human activity. In particular, the toxicity of cadmium for plants, animals and human life is well documented by several studies that have been carried out. Among the environmental trace elements, cadmium presents the most insidious and widespread health hazard. When inhaled, cadmium completely absorbs in the lungs; it is also known that not only cadmium induces arterial hypertension and affects on the kidneys, but also some toxic effects attributed in the past to lead (proteinuria) [1–3].

Consequently, the development of reliable methods for the removal and determination of cadmium in environmental samples is a significant subject. Among the spectral methods, FAAS method is simple, rapid, reliable, low cost and present in almost all analytical laboratories. On the other hand, FAAS is highly selective (as atomic lines are sharp) but not that sensitive compared to widely accepted and costlier ICP-MS, ICP-AES and GF-AAS. Hence, combining a preconcentration step prior to FAAS determination is often resorted by various researchers [4–9]. In recent years, differ-

ent preconcentration techniques such as coprecipitation [10] and solid-phase extraction [11–13] have been used for analyte sample enrichment.

Solid-phase extraction of traces of heavy metal ions is widely used in preconcentration methodology. Batch and column procedures are the two important parts of the solid-phase extraction. Various solid materials such as activated carbon [14], cellulose [15], naphthalene [16], amberlite XAD-2 resin [17], Polymeric adsorbent resin [18] and synthetic zeolites [19] have been used for solid-phase extraction. Some of these adsorbents are suitable for preconcentration of metal ions, but their methods of preparation are time-consuming and involve rigid control of conditions.

Natural zeolites have been intensively studied recently because of their applicability in removing by utilizing the ion exchange phenomenon [20–24]. The main reason of the interest for natural zeolite-bearing materials is the increasing demand of low-cost ion exchange and adsorbent materials in such fields as energy production, pollution control and metal recovery as well as their wide availability on the earth [25].

Clinoptilolite with the simplified formula $(\text{Na}, \text{K})_6 \text{Si}_{30} \text{Al}_6 \text{O}_{72} \cdot n\text{H}_2\text{O}$ is the most abundant natural zeolite and may serve as cost-effective sorbent. Although clinoptilolite is commonly used as a cation exchanger, it can be modified to increase its total organic carbon content in order to enhance sorption of anionic and organic compound [26,27].

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In the present paper an attempt is made to investigate the adsorption of cadmium ions from real water and plant samples on surfactant modified clinoptilolite loaded with neothorin. The significance of this work is the possibility of using a cheap natural adsorbent for concentration of trace amounts of cadmium ions in a regime of solid-phase extraction. Moreover, in our study, it is aimed to investigate the thermodynamic of adsorption and obtain the best conditions for maximum removal of cadmium.

2. Experimental

2.1. Apparatus

A Varian model spectrAA220 flame atomic absorption spectrometer was used for the analysis. The instrumental conditions were selected as suggested by manufacturer (current: 4.0 mA, wavelength: 228.3 nm, the bandwidth of the slit: 0.5 nm). The flame composition was acetylene with a flow rate of 2.0 L min⁻¹ and air with a flow rate of 10.0 L min⁻¹. The suggested flow rate for Nebulizer ranges between 4 and 6 mL min⁻¹. The 5.0 mL min⁻¹ was used for all experiments. A metrohm 713 pH meter (Switzerland) was employed for pH measurements. For preconcentration procedures a glass column (500 mm × 10 mm) equipped with Teflon tap was used.

2.2. Reagents and solutions

Cadmium nitrate (Merck, Darmstadt, Germany) solution was prepared by dissolving the analytical grade sample in distilled water and standardized by known methods. A 0.001 mol L⁻¹ solution of neothorin (Fluka, Steinheim, Germany) in distilled water was prepared. Benzyltrimethyltetradecylammonium chloride (BDTA, 98% purity, Merck) dissolved in distilled water to obtain a 0.050 mol L⁻¹ solution. Alkali metal and various metal (Merck) solutions were used for studying of anionic and cationic interferences. Buffer solution of pH, 4–5.5, was prepared by mixing 0.1 mol L⁻¹ sodium acetate and 0.1 mol L⁻¹ acetic acid solutions in appropriate ratio. Natural clinoptilolite zeolite was obtained from Semnan region in the center of Iran.

2.3. Zeolite modification

The clinoptilolite tuff was ground and sieved to a size range of 0.110–0.125 mm. Prior to use, the zeolite was treated with 100 mL of 1 mol L⁻¹ of sodium acetate/acetic acid buffer (pH 5) and then rinsed with water to remove any residual carbonate. The pretreated minerals were dried at 60 °C overnight and stored in polyethylene containers. The ammonium ion has a high affinity for clinoptilolite and it can be used to replace other cations. Thus, H-clinoptilolite was prepared from the ammonium form of clinoptilolite by calcination at 380 °C for 2 h [28–30].

Clinoptilolite was saturated with zinc to obtain a uniform substrate and avoid entrance of analyte into pores of zeolite after elution with HNO₃ by shaking 10 g of clinoptilolite for 2 h with 100 mL of 100 µg L⁻¹ zinc solution. This was followed by 2 rinses with 4 mol L⁻¹ nitric acid and 3 rinses with distilled water and finally a drying stage is imposed onto them.

Natural zeolites have negatively charged surfaces that can be modified by cationic surfactants to increase their total organic carbon in order to enhance sorption of nonionic organic compound. The zinc-saturated clinoptilolite was modified with BDTA. Surfactant modification consisted of 10 g of clinoptilolite with 250 mL of the BDTA solution (0.050 mol L⁻¹) for 24 h at 25 °C. It is shown that this time is sufficient for complete reaction of BDTA on clinoptilolite. The BDTA-modified clinoptilolite was placed on a paper filter

in a büchner funnel, rinsed with 30–50 mL of distilled water and air-dried.

A glass column (500 mm height × 10 mm internal diameter) equipped with Teflon tap was loaded with 1.00 g of the modified clinoptilolite. Then 4 mL of 0.001 mol L⁻¹ solution of neothorin was passed through it at flow rate of 1 mL min⁻¹. Prior to sample loading, the column was preconditioned by passing a buffer solution.

2.4. Procedure for the sorption of cadmium on the column

An aliquot of the solution containing 0.05–20 µg of cadmium was taken in a beaker and 2.0 mL of buffer solution with pH 5 was added to it and then diluted to 50 mL with distilled water. This solution was passed through the column at flow rate 1.0 mL min⁻¹. After passing this solution, the column was washed with 3 mL of distilled water. The adsorbed cadmium on the column was eluted with 5.0 mL of 2.5 mol L⁻¹ nitric acid, at flow rate 0.7 mL min⁻¹. The eluent was collected in a 5.0 mL volumetric flask and cadmium was determined by flame atomic absorption spectrometry.

2.5. Sorption isotherm models

Analysis of equilibrium data is important for developing an equation that can be used to compare different materials under different operational conditions. Moreover, it is used to design and optimize an operating procedure [31].

The sorption equilibrium data for Cd on modified clinoptilolite zeolite is analyzed in terms of the Freundlich and Langmuir isotherm models. The relative coefficients of these models were calculated using linear least-squares fitting. The Freundlich isotherm based on sorption on a heterogeneous surface is as follows [32]:

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

where q_e is the amount adsorbed at equilibrium (µg g⁻¹) and C_e is the equilibrium concentration (mg L⁻¹). K_F and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively. The linearized form of Freundlich sorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

By plotting $\ln q_e$ versus $\ln C_e$, K_F and n can be determined if a straight line is obtained.

The Langmuir sorption isotherm $q_e = (q_m b C_e)/(1 + b C_e)$ on linearization becomes: $C_e/q_e = (C_e/q_m) + (1/q_m b)$ where q_e is the amount adsorbed at equilibrium (mg g⁻¹), C_e the equilibrium concentration (mg L⁻¹), b a constant related to the energy or net enthalpy of adsorption (L mg⁻¹) and q_m is the maximum adsorption capacity (mg g⁻¹). By plotting C_e/q_e versus C_e , q_m and b can be determined.

3. Results and discussion

3.1. General results

Influence of pH on extraction of cadmium is shown in Fig. 1. Based on the results, the maximum sorption is in the pH range of 4.0–6.2. In subsequent studies, the pH was maintained at approximately 5. At pH values below 4.0 the concentration of hydroxonium ions in the solution would be high and prevent any adsorption onto the active sites on the substrate surface. Similarly, in basic solution (pH > 7) the concentration of OH⁻ ions would be high, leading to precipitation of the cations as their corresponding hydroxides rather than their adsorption on to the adsorbent surface. The effect of sample flow rate was also examined under the optimum conditions. The flow rates were adjusted in range of 0.2–3.0 mL min⁻¹.

Table 1
Comparative data from some recent studied on pre-concentration of cadmium.

Adsorbent/complexing media	Pre-concentration factor	Detection limit ($\mu\text{g L}^{-1}$)	Relative standard deviation (%)	Reference
Cloud point extraction/dithizone and triton X-114	52	0.31	2.4	[33]
Amberlite XAD-2/2-aminothiophenon	28	0.14	2.1	[34]
Chromosorb 108/bathocuproinedisulfonic acid	80	0.24	1.4	[35]
Amberlite XAD-4/5-Br-PADAP	110	6	1.3	[36]
Cloud point extraction/Triton X-114	55.6	1	1.3	[37]
Amberlite XAD-2-PC resin/pyrocatechol	16	0.77	2.1	[38]
Clinoptilolite/neothorin	160	0.015	0.94	Present work

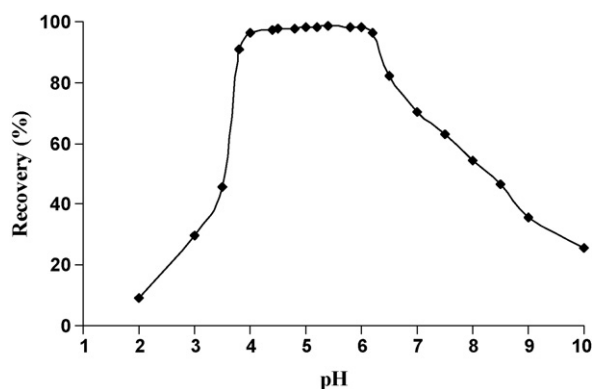


Fig. 1. Effect of pH on the recoveries of cadmium ions on modified clinoptilolite.

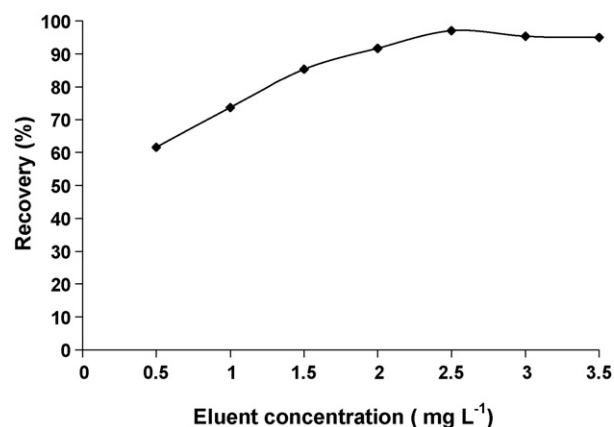


Fig. 3. Effect of eluent concentration on the recoveries of cadmium.

In all experiments, the quantitative recoveries of the metal ions decreased while the flow rate increased. A flow rate of 1 mL min^{-1} was recommended in all experiments (Fig. 2). The volume of the aqueous phase was varied in the range of 100–1000 mL under optimum conditions, keeping the other variable constant. It was observed that the absorption was almost constant up to 800 mL. The pre-concentration factor is calculated as the ratio of the highest sample volume (800 mL) to the lowest eluent volume (5.0 mL). The pre-concentration factor was obtained 160. The pre-concentration factor achieved with the presented modified clinoptilolite for cadmium is better than all the other important chelating matrices (Table 1).

Preliminary observation indicated that cadmium was desorbed completely with 5.0 mL of 2.5 mol L^{-1} nitric acid. Therefore, 5.0 mL of 2.5 mol L^{-1} nitric acid was used in the present work (Fig. 3).

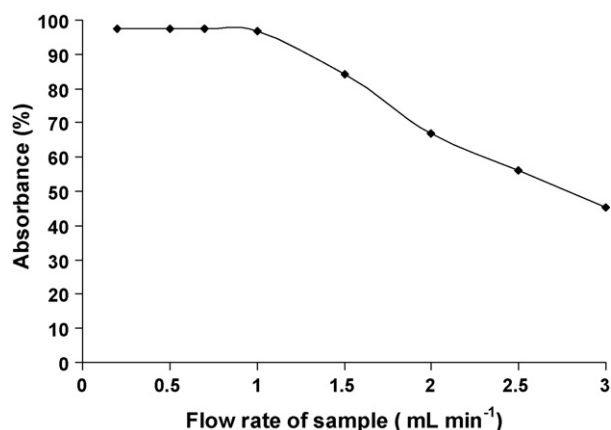


Fig. 2. Effect of the sample flow rates on the sorption of cadmium.

3.2. Adsorption capacity of modified clinoptilolite

For evaluating the adsorption capacity of modified clinoptilolite for cadmium several $5.0 \mu\text{g mL}^{-1}$ cadmium solutions were passed through the column. The outlet solutions were collected and the presence of cadmium was tested in each of them by FAAS, respectively. When cadmium was detected in one of the solutions, the test was ceased and the adsorption capacity was calculated. The adsorption capacity was obtained 0.50 mg cadmium per each gram of modified clinoptilolite.

3.3. Calibration and sensitivity

$0.05 \mu\text{g}$ of cadmium was retained by passing 800 mL of solution through the column. Calibration curve is linear in the $0.01\text{--}4 \mu\text{g mL}^{-1}$ in final solution with correlation factor of 0.999. Also the calibration equation is $A = 0.1515C (\mu\text{g mL}^{-1}) + 0.0032$ (Fig. 4). Eight replicate determination of $7.5 \mu\text{g}$ cadmium in final

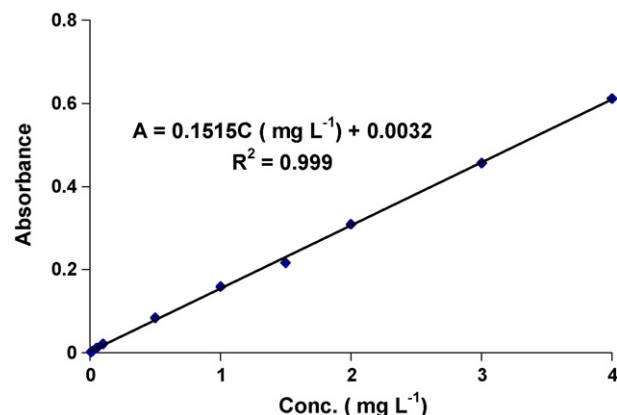


Fig. 4. Calibration curve.

Table 2
Effect of diverse ions on the cadmium determination.

Ions	Tolerance limit (mg)	Mass ratio (mg interference/mg Cd)
CH ₃ COO ⁻	500	6.7 × 10 ³
S ²⁻	200	2.7 × 10 ³
F ⁻	50	6.7 × 10 ³
Cl ⁻	30	4 × 10 ³
HCO ₃ ⁻	10	1.3 × 10 ³
SO ₃ ²⁻	75	10 × 10 ³
Ca ²⁺	36	4.8 × 10 ³
Tl ³⁺	10	1.3 × 10 ³
Na ⁺	115	15 × 10 ³
Pb ²⁺	7.5	1000
Tl ⁺	5	666
Bi ³⁺	4	533
Cr ³⁺ , Ce ⁴⁺ , Mn ²⁺	3	400
Al ³⁺	2.5	333
Ni ²⁺ , Mg ²⁺	2	266
Sn ²⁺ , Co ²⁺ , Cu ²⁺	1.5	200
Au ³⁺	0.05	6.66

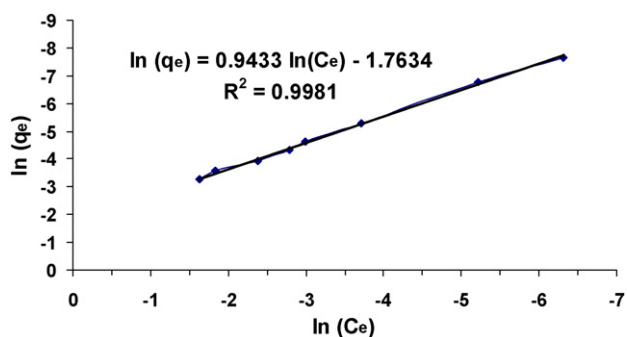


Fig. 5. Freundlich sorption isotherm of cadmium at pH 5.

solution gave a mean absorbance of 0.2154 with a relative standard deviation of $\pm 0.94\%$. Sensitivity for 1% absorbance was 7.92 ng mL^{-1} .

3.4. Effect of diverse ions

The potential interference in the present method has been investigated. The interference is due to the competition of other heavy metal ions for the chelating agent and their subsequent co-extraction with cadmium. For examining the probability of interferences, a fixed amount of cadmium ions was taken with different amounts of foreign ions, and the recommended procedure was followed. The recovery of cadmium in these experiments was 97%. The tolerance limit was as the amount of each ion that require for causing $\pm 3\%$ error in the determination of cadmium (Table 2).

3.5. Sorption isotherms

Variation of initial cation concentration was studied at room temperature. The sorption data were analyzed in terms of the Freundlich and Langmuir isotherm models.

The isotherm plot for Cd isothermal adsorption data is shown in Fig. 5. It demonstrates that the Freundlich adsorptive isothermal equation fits the experimental data well. K_F and n were calculated 0.171 and 1.06 for Cd, respectively.

Values of K_F derived from the Freundlich theory are an indicator of the adsorption capacity of a given adsorbent. The exponent n was greater than unity which indicates a favorable adsorption process.

Table 3
Analysis of cadmium in plant samples.

Sample	Cadmium found ^a ($\mu\text{g g}^{-1}$) by present method
Leaf of pistachio	2.24 \pm 0.01
Stem of pistachio	3.04 \pm 0.03
Stem of beet	3.74 \pm 0.04
Blossom of beet	3.49 \pm 0.02

^a Mean of five determinations, \pm standard deviation, after preconcentration of cadmium by present method.

Table 4
Analysis of cadmium in water samples^a.

Water samples	Cadmium found ^b by present method (mg L^{-1})
Well water ^c	1.52 \pm 0.06
Drinking water ^d	1.22 \pm 0.04
Waste water ^c	3.15 \pm 0.05
Filtered waste water ^c	2.1 \pm 0.10

^a Sample volume: 100 mL and final volume: 5 mL.

^b Mean of five determinations, \pm standard deviation after preconcentration of cadmium by present method.

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^d Kerman, Iran.

3.6. Determination of cadmium in plant samples

The applicability of the proposed method was evaluated in plant samples. Various plant samples were dried in 80°C for 72 h. 0.1 g of the samples (pistachio and beet) was individually taken in a beaker and dissolved in concentrated nitric acid and perchloric acid (3:1) by heating on a hot plate. The solution was cooled, diluted and if needed filtered. The filtered solution was diluted to 100.0 mL with distilled water in a calibration flask. A 50 mL of the pretreated sample solution was taken and analyzed by the procedure that explained in Section 2.4. The related results are presented in Table 3. Results show that this procedure is a good method for determination of low level of cadmium in plant samples.

3.7. Determination of cadmium in water samples

The proposed method was applied to the determination of cadmium in water samples. A 95 mL of water sample was filtered to remove suspended materials. The filtered solution was made to 100.0 mL with buffer solution and distilled water. A 50 mL of solution was passed through the column and analyzed by general procedure (Table 4).

4. Conclusion

The present method was successfully applied to extraction and preconcentration of cadmium and its determination by FAAS. The adsorption data were analyzed in terms of the Langmuir and Freundlich isotherm models and the data fit the Freundlich sorption isotherm. A comparison of the proposed method was done with other preconcentration procedures using several sorbents. Preconcentration factor for this procedure was 160. Thus, it is comparable to those presented by other methods described in the literature. Low detection limit, low relative standard deviation and high tolerance to interferences from matrix ions allow the application of the new proposed sorbent for Cd determination in water and plant samples. The good features of the proposed method showed that this method is a convenient and low cost one.

Based on results, zeolite modified with surfactant and neothorin is fairly sensitive and selective for cadmium. Moreover, the preconcentration step and utilizing of atomic absorption spectrometry improve its sensitivity and selectivity.

References

- [1] M.D. Petit, M.I. Rucanido, Sequential extractions for determination of cadmium distribution in coal fly ash, soil and sediment samples, *Anal. Chim. Acta* 401 (1999) 283–291.
- [2] K.J. Brodie, J.P. Matousek, Determination of cadmium in air by non-flame atomic absorption spectrometry, *Anal. Chim. Acta* 69 (1974) 200–202.
- [3] E. Helmers, Speciation of cadmium in seawater—a direct voltammetric approach, *Fresenius J. Anal. Chem.* 350 (1994) 62–67.
- [4] A.J. Buchet, M. Witzensbacher, Pesticide monitoring of drinking water with the help of solid-phase extraction and high-performance liquid chromatography, *J. Chromatogr. A* 737 (1996) 67–74.
- [5] J.S. Fritz, *Analytical Solid Phase Extraction*, first ed., Wiley–VCH, New York, USA, 1999.
- [6] D. Atanassova, V. Stefanova, E. Russeva, Flame atomic absorption spectrometric determination of silver after preconcentration on Amberlite XAD-16 resin from thiocyanate solution, *Talanta* 51 (2001) 889–894.
- [7] M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, A. Najibi, M. Soyulak, Cloud point extraction and flame atomic absorption spectrometric determination of cadmium(II), lead(II), palladium(II) and silver(I) in environmental samples, *J. Hazard. Mater.*, in press.
- [8] M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A.S. Mirsadeghi, A. Pourfarokhi, M. Soyulak, The determination of some heavy metals in food samples by flame atomic absorption spectrometry after their separation–preconcentration on bis salicyl aldehyde, 1,3 propan diimine (BSPDI) loaded on activated carbon, *J. Hazard. Mater.* 154 (2008) 128–134.
- [9] M. Ghaedi, M.R. Fathi, F. Marahel, F. Ahmadi, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, *Fresenius Environ. Bull.* 14 (2005) 1158–1163.
- [10] K. Prasad, P. Gopikrishna, R. Kala, T. Prasada Rao, G.R.K. Naidu, Solid phase extraction vis-à-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.
- [11] N. Pourreza, H. Zavvar Mousavi, Determination of cadmium by flame atomic absorption spectrometry after preconcentration on naphthalene–methyltriethylammonium chloride adsorbent as tetraiodocadmiate (II) ions, *Anal. Chim. Acta* 503 (2004) 279–282.
- [12] M.A. Taher, E. Rezaei pour, D. Afzali, Anodic stripping voltammetric determination of bismuth after solid-phase extraction using amberlite XAD-2 resin modified with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, *Talanta* 63 (2004) 797–801.
- [13] H. Serencam, A. Gundogdu, U. Yygur, B. Kemer, V.N. Bulut, C. Duran, M. Soyulak, M. Tufekci, Removal of cadmium from aqueous solution by Nordmann fir (*Abies nordmanniana* (Stev.) Spach. Subsp. nordmanniana) leaves, *Bioresour. Technol.* 99 (2008) 1992–2000.
- [14] M.B. Gholivand, F. Ahmadi, E. Rafiee, Solid phase extraction and determination of ultra trace amounts of copper using activated carbon modified by N,N'-bis(salicylidene)-1,2-phenylenediamine, *Sep. Sci. Technol.* 42 (2007) 897–910.
- [15] P. Burba, P.G. Willmer, Cellulose: a biopolymeric sorbent for heavy-metal traces in waters, *Talanta* 30 (1983) 381–383.
- [16] M.A. Taher, Flame atomic absorption spectrometric determination of trace amounts of manganese in alloys and biological samples after preconcentration with the ion pair of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and ammonium tetraphenylborate on microcrystalline naphthalene or by column method, *Anal. Sci.* 17 (2001) 969–973.
- [17] S.L.C. Ferreria, C.F.D. Brito, A.F. Danats, M. Neyla Lopo de Araújo, A.C. Spinola Costa, Nickel determination in saline matrices by ICP-AES after sorption on Amberlite XAD-2 loaded with PAN, *Talanta* 48 (1999) 1173–1177.
- [18] E. Melek, M. Tuzen, M. Soyulak, Flame atomic absorption spectrometric determination of cadmium(II) and lead(II) after their solid phase extraction as dibenzylthiocarbamate chelates on Dowex Optipore V-493, *Anal. Chim. Acta* 578 (2006) 213–219.
- [19] Y.P. Pena, W. Lopez, J.L. Burguera, M. Burguera, M. Galignani, R. Brunetto, P. Carrero, C. Randon, F. Imbert, Synthetic zeolites as sorbent material for on-line preconcentration of copper traces and its determination using flame atomic absorption spectrometry, *Anal. Chim. Acta* 403 (2000) 249–258.
- [20] D. Afzali, M.A. Taher, A. Mostafavi, S.Z. Mohammadi Mobarakeh, Thermal modified Kaolinite as useful material for separation and preconcentration of trace amounts of manganese ions, *Talanta* 65 (2005) 476–480.
- [21] M.A. Taher, A. Mostafavi, D. Afzali, E. Rezaei Pour, Anodic stripping differential pulse voltammetric determination of trace amounts of lead after preconcentration of its complex with 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol onto natural analcime zeolite by column method, *Bull. Korean Chem. Soc.* 25 (2004) 1125–1129.
- [22] A. Shanableh, A. Kharabsheh, Stabilization of Cd, Ni and Pb in soil using natural zeolite, *J. Hazard. Mater.* 45 (1996) 207–217.
- [23] P. Misaelides, A. Godelitsas, V. Charistos, D. Ioannou, D. Charistos, Heavy metal uptake by zeoliferous rocks from Metaxades, Thrace, Greece: an exploratory study, *J. Radioanal. Nucl. Chem.* 183 (1994) 159–166.
- [24] S. Hajjaligol, M.A. Taher, A. Malekpour, Determination of trace amounts of zinc by flame atomic absorption spectrometry after preconcentration with modified clinoptilolite zeolite, *J. AOAC Int.* 91 (2008) 1446–1452.
- [25] A. Cincotti, N. Lai, R. Orru, G. Cao, Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modeling, *Chem. Eng. J.* 84 (2001) 275–282.
- [26] Z. Li, Chromate extraction from surfactant-modified zeolite surfaces, *J. Environ. Qual.* 27 (1998) 240–242.
- [27] H.T. Shu, D. Li, A.A. Scala, Y.H. Ma, Adsorption of small organic pollutants from aqueous streams by aluminosilicate-based microporous materials, *Sep. Purif. Technol.* 11 (1997) 27–36.
- [28] E. Chmielewska-Horvathova, J. Lesny, Iodide adsorption on the surface of chemically pretreated clinoptilolite, *J. Radioanal. Nucl. Chem.* 200 (1995) 351–363.
- [29] S.K. Milonjic, T.S. Ceranic, M.Dj. Petkovic, A gas chromatographic study of the adsorption of organics on thermally treated clinoptilolite, *Chromatographia* 27 (1989) 306–310.
- [30] S. Hajjaligol, M.A. Taher, A. Malekpour, A new method for the selective removal of cadmium and zinc ions from aqueous solution by modified clinoptilolite, *Adsorp. Sci. Technol.* 24 (2006) 487–496.
- [31] L. Lv, G. Tsoi, X.S. Zhao, Uptake equilibrium and mechanism of heavy metal ions on microporous titanosilicate ETS-10, *Ind. Eng. Chem. Res.* 43 (2004) 7900–7906.
- [32] H.M.F. Freundlich, Über die adsorption in lösungum, *Z. Phys. Chem.* 57 (1906) 385–470.
- [33] J.L. Manzoori, G. Karim-Nezhad, Development of a cloud point extraction and preconcentration method for Cd and Ni prior to flame atomic absorption spectrometric determination, *Anal. Chim. Acta* 521 (2004) 173–177.
- [34] V.A. Lemos, P.X. Baliza, Amberlite XAD-2 functionalized with 2-aminothiophenol as a new sorbent for on-line preconcentration of cadmium and copper, *Talanta* 67 (2005) 564–570.
- [35] M. Tuzen, M. Soyulak, L. Elci, Multi-element pre-concentration of heavy metal ions by solid phase extraction on Chromosorb 108, *Anal. Chim. Acta* 548 (2005) 101–108.
- [36] M.A. Taher, A. Mostafavi, S.Z. Mohammadi Mobarake, D. Afzali, Simultaneous separation and preconcentration of trace amount of copper, nickel, cadmium and zinc ions onto modified amberlite XAD-4 loaded with 5-Br-PADAP, *Bull. Chem. Soc. Ethiopia* 20 (2006) 1–8.
- [37] A. Afkhami, T. Madrakian, H. Siampour, Flame atomic absorption spectrometric determination of trace quantities of cadmium in water samples after cloud point extraction in Triton X-114 without added chelating agents, *J. Hazard. Mater.* 138 (2006) 269–272.
- [38] V.A. Lemos, D.G. da Silva, A.L. de Carvalho, D.A. Santana, G.S. Novaes, A.S. dos Passos, Synthesis of amberlite XAD-2-PC resin for preconcentration and determination of trace elements in food samples by flame atomic absorption spectrometry, *Microchem. J.* 84 (2006) 14–21.