

Application of Ion - Imprinted Polymer Synthesized as New Sorbent for Preconcentration and Separation of Thallium (I) and Its Determination by Electrothermal Atomic Absorption Spectroscopy

Darroudi, Abolfazl*⁺

*Department of Chemistry, Faculty of Samen Hojaj, Mashhad Branch, Technical and Vocational University (TVU),
Tehran, I.R. IRAN*

Chamsaz, Mahmoud; Arab Zavar, Mohammad Hossein

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, I.R. IRAN

Zakeri Mofrad, Issa

*Department of Chemistry, Faculty of Samen Hojaj, Mashhad Branch, Technical and Vocational University (TVU),
Tehran, I.R. IRAN*

ABSTRACT: At this study, thallium (I) ion-imprinted polymer, as a novel sorbent for Tl (I) and comparison with Tl(III) ion-imprinted polymer has been synthesized. This sorbent for preconcentration and solid-phase extraction of Tl(I) ions from aqueous solutions, used. Through preparing the binary complex of Tl(I) ions with 5, 7-dichloroquinoline-8-ol (DCQ) the particles of thallium (I) Ion-Imprinted Polymer (IIP) have synthesized. In the presence of 2-methoxyethanol (porogen) and 2, 2'-azobisisobutyronitrile (initiator, AIBN) Thermal copolymerization of methyl methacrylate (functional monomer, MMA) and ethyleneglycoldimethacrylate (cross-linking monomer, EGDMA) have done. The imprinted ion has removed from the polymer by removing the above particles with 1 mol/L HNO₃ to obtain the leached IIP particles. Similarly, Control Polymer (CP) particles, have prepared without thallium (I) ions. The characterization of unleached and leached IIP particles was done by, Fourier-Transform InfraRed (FT-IR) spectroscopy, Brunauer-Emmett-Teller (BET), surface area analysis, and X-Ray Diffraction (XRD). As a function of pH, the preconcentration of thallium (I) has studied during rebinding with the leached IIP particles, for determination of thallium in aqueous solution, the weight of the polymer material, the elution and preconcentration times, the concentration of eluent (nitric acid), the volume of the aqueous phase and the volume of an eluent. ElectroThermal Atomic Absorption Spectrometry (ETAAS) has utilized. The method's Detection limit was 0.1 mg/ mL, while the relative standard deviation for five times repeat was 3.5%.

KEYWORDS: Thallium (I); Ion-imprinted polymer; Sorbent; electrothermal atomic absorption spectroscopy.

* To whom correspondence should be addressed.

+ E-mail: abf_mashhad@yahoo.com

1021-9986/2020/1/59-66

8/\$/5.08

INTRODUCTION

Recently it has reported that ion imprinting method as a potential tool for preparing highly selective polymeric materials, applied in the Pre-concentration and extraction of different ions such as: Cd^{2+} [1,2], Ce^{3+} [3], Co^{2+} [4], Cr(VI) [5], Cs^+ [6], Cu^{2+} [7-9], Fe^{3+} [10], Hg^{2+} [11,12], Ni^{2+} [13], Pb^{2+} [14,15], Pd^{2+} [16], Ru^{3+} [17], Sb^{3+} [18,19], Sm^{3+} [20], Tl^{3+} [21,22], UO_2^{2+} [23-25] and Zn^{2+} [26]. Tl is well known, for its carcinogenic, mutagenic and teratogenic effects [27]. In nature thallium founded as Tl(I) and Tl(III) ions however its monovalent state has more stability, while its trivalent state; produce a complexes with better stability. Each elemental oxidation state exhibits different toxicity and bioavailability feature therefore, thallium speciation in the environment is so important [21]. The determination of Tl(I) is of great interest because of its clinical and environmental roles and also industrial applications. The amount of thallium in geological and environmental samples is lower than the detection limits of most of analytical methods. Thus, the extraction, Pre-concentration, and determination of trace thallium (I) from the natural water resources are so necessary and require more consideration. Tl(I) is highly toxic to the biosphere even more than Hg, Cd, Pb and Cu [28].

In this study, a thallium (I) ion-imprinted polymer (IIP) as a new sorbent has been synthesized for Tl(I) ion and also compared with Tl(III) ion imprinted polymer with different pH and stoichiometry. This sorbent was used for extraction of Tl(I) in different water samples.

EXPERIMENTAL SECTION

Instrumentation

A Shimadzu model AA-670 atomic absorption spectrometer with GFA-4B Graphite Furnace Atomizer (GFA) with a D_2 lamp for background correction was used for determination of thallium. A thallium hollow cathode lamp, adjusted at 5 mA, was used as the radiation source. Measurements were carried out in peak height mode at 276.8 nm, using a spectral bandwidth of 0.5 nm. The atomic absorption signal at 276.8 nm was recorded on a graphic printed PR-4, and the height of the peak was used for determination of thallium. The temperature program for the furnace has been given in a previous work [28]. A sampler (Ependorf, Germany) was applied to inject 20 μL of the solution into the graphite tube. An F20520162 Velp Scientifica magnetic stirrer (Italia)

was employed to stir the sample solution. The FT-IR spectra ($4000\text{--}400\text{cm}^{-1}$) using KBr were recorded with the aid of a MB-154 model Bomem spectrometer. The XRD patterns were obtained with X-ray of 1.54056 \AA wavelength by a $\text{Cu K}\alpha$ X-ray source and a Philips PW1710 diffractometer (The Netherlands). pH values were measured with a Metrohm model 632 pH-Meter. The surface area analysis was carried out by using Quantachrome autosorbe-1 surface area analyzer (USA). An Agilent model 8453 UV-Visible spectrophotometer was employed to prepare the UV-Vis spectrum of the reaction mixtures

Reagents and materials

All reagents were of analytical reagent grade and deionized water was used throughout. A stock Tl(I) solution ($1000\mu\text{g}/\text{mL}$) was prepared by dissolving TlNO_3 (Merck) and dilution to 100mL with deionized water. 5, 7-Dichloroquinoline-8-ol was obtained from Acros organics, New Jersey, USA, methylmethacrylate, ethylene glycoldimethacrylate and 2, 2-azo bis isobutyronitrile (AIBN) were obtained from Merck. Moreover, stock solutions of KNO_3 , NaNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2$ ($1000 \mu\text{g}/\text{mL}$ each) were prepared (Merck).

Synthesis of the thallium(I) IIP materials

The Tl(I) binary complex was prepared by dissolving 1mmol Tl(I) nitrate (0.263 g) in 5mL of 2-methoxyethanol. This mixture was then added drop wise while stirring to a solution of 2.0 mmol 5, 7-dichloroquinoline-8-ol (0.44 g) in 5mL of 2-methoxyethanol. The resulting orange solution was stirred for 1 h in order to complete the reaction. UV-Visible spectral studies, mole ratio plot (data are available on request) confirmed the formation of binary complex that the mole ratio of thallium to DCQ is 1:2.

The above complex solution was mixed with 5mmol of MMA (0.500 g), 20mmol of EGDMA (4.20 g) and 100 mg of AIBN. This solution was stirred for about 20 min until a homogeneous solution was attained. The prepared solution was cooled to $0 \text{ }^\circ\text{C}$, purged with Argon (99.999%) for 10 min, sealed and heated at 55°C during stirring for 24 h. The obtained particles were grounded in a mortar and dried in a hot air oven at $60 \text{ }^\circ\text{C}$ for 5 h and sieved to acquire the powdered particles.

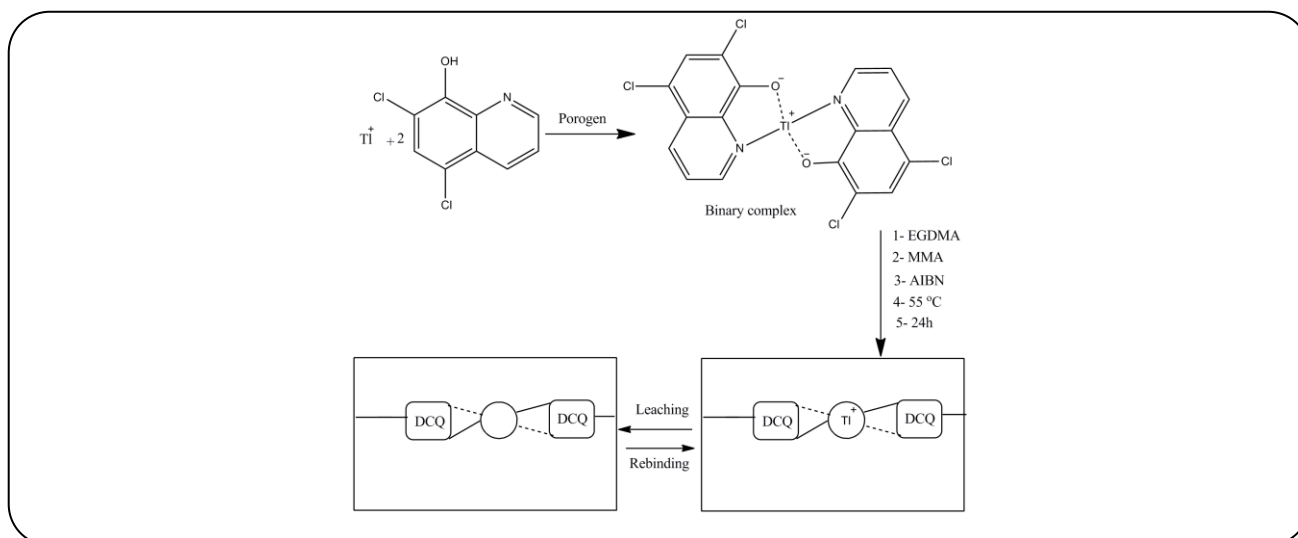


Fig. 1: Proposed schematic representation of the ion-imprinted polymer process.

About 3 g of these powdered particles were subjected to leaching with 200 mL of 5 mol/L HNO_3 for 5 h to obtain thallium IIP particles. The control polymer (CP) particles were prepared in a similar way as that of the IIP preparation, but without the imprinted ion, thallium (I). The resultant CP particles were compared with IIP particles in terms of extraction ability. The proposed schematic representation of ion-imprinted polymer synthesis is given in Fig. 1.

Analytical procedures

The extraction studies of the Tl^{+} ions with the prepared imprinted polymer were carried out by batch experiments as follows: Aliquots of Tl^{+} solution (50 mL) in the concentration range 1-500 ng/mL was treated with 150 mg of polymer particles at various pHs and stirred for 35 min with the use of a magnetic stirrer. The pH value was adjusted to 7 ± 0.2 by adding sodium hydroxide or nitric acid.

The Tl^{+} ions were eluted from the IIP particles using 5 mL of 1.0 mol/L nitric acid, through a filter paper. Their content in the eluent was determined with ETAAS at 276.8 nm.

RESULTS AND DISCUSSION

Characterization studies

X-Ray Diffraction (XRD)

The XRD patterns of the unleached (a) and leached (b) IIP particles are given in Fig. 2. It showed that the thallium was only present in the unleached polymer particles and it was completely removed after leaching.

FT-IR spectra

The IR spectra of unleached and leached $Tl(I)$ imprinted polymers were recorded using KBr pellet method (Fig. 3). It is obvious that these polymers have the same backbone; (3487.41 cm^{-1} for OH; 2947.42 cm^{-1} for aromatic and aliphatic CH; 1726.1 cm^{-1} for C=O; 1450.3 cm^{-1} for aromatic ring and 1143.7 cm^{-1} for C-O). The broad absorption at 3487.41 cm^{-1} due to -OH stretching is weakened in unleached. This is due to the interaction of the deprotonated -OH group of DCQ with $Tl(I)$. The peak near 756 cm^{-1} corresponded to ν_{C-Cl} in the spectra of both the leached and unleached polymers, illustrating that DCQ was kept intact in the polymer even after leaching.

Nitrogen sorption

The synthesized IIP particles were characterized using nitrogen sorption studies, in order to know the surface properties of the leached and control polymer particles. The surface area was determined by applying the BET equation. The surface area (m^2/g) is: 225 for IIP and 190 for CP. Pore size analysis shows an average pore diameter of 18 \AA . These data indicate the formation of polymer particle with nano-pore and excessive surface area.

Optimization of sorption and elution of Tl^{+} ion using IIP particles employing batch method

In order to optimize conditions for obtaining high efficiency in preconcentration of $Tl(I)$ ions by the proposed IIP, it is necessary to adjust several factors

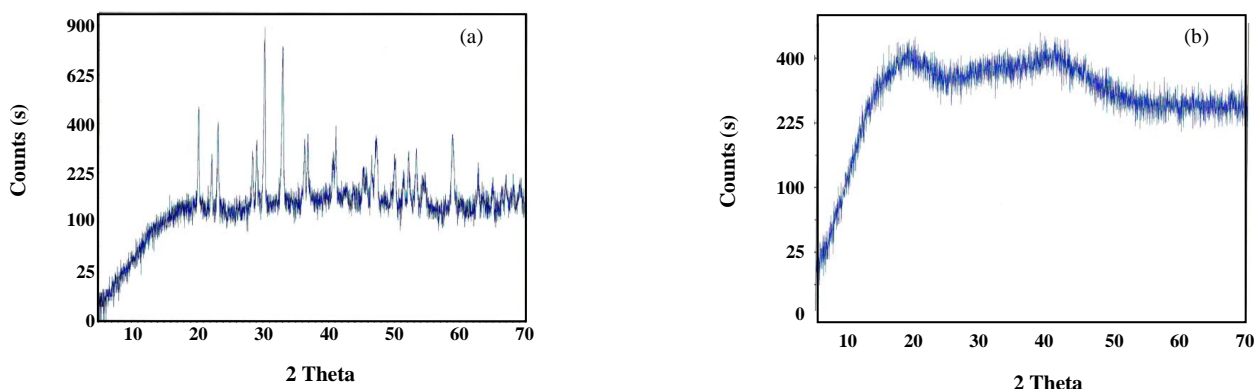


Fig. 2: XRD patterns of unleached (a) and leached (b) thallium IIP particles.

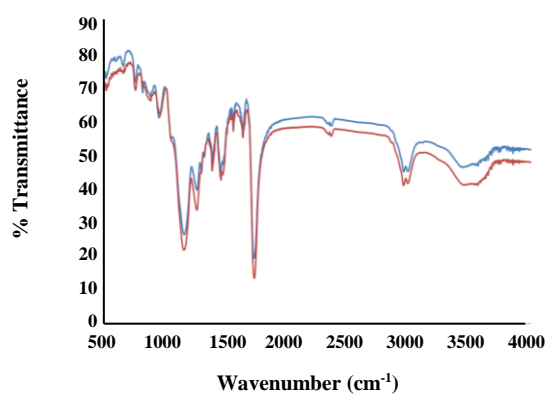


Fig. 3: FT-IR spectra of the leached and unleached IIP particles.

including pH, sample volume, HNO_3 concentration, eluent volume, preconcentration, and elution time. The percentage recovery of thallium ions was calculated from the ETAAS results.

Effect of pH

A series of solutions with the volume of 50 mL and thallium concentration of 50 ng/mL were prepared. The pH values of these solutions were adjusted between 4.0 to 8.0. The extraction percentage of IIP particles increases with the increase in pH, as can be seen in Fig. 4. The increase in extraction percentage in the pH range of 4.0–7.0 for IIP particles is attributed to the competition of Tl(I) ions with H^+ ions which forms a complex with 5,7-dichloroquinoline-8-ol. On the other hand, the extraction percentage is constant at pHs greater than 7. In the subsequent work, the pH was adjusted to 7.0 ± 0.2 .

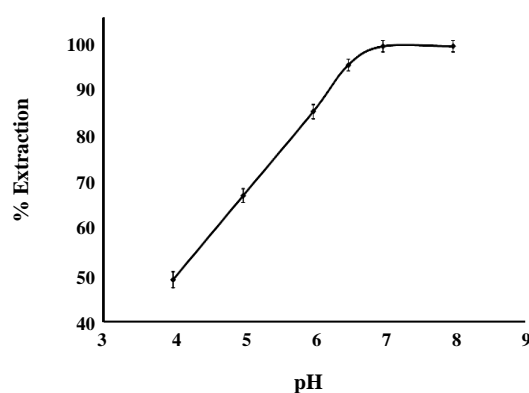


Fig. 4: pH effect on the uptake of the thallium ions using leached IIP particles.

Optimization of other experimental variables

All the other parameters influencing the preconcentration of Tl(I) ions with IIP particles were systematically evaluated. The corresponding results are recorded in Table 1. It can be seen that the best condition for preconcentration occurs at about 0.15 ± 0.02 g of polymer particles used at pH 7. The effect of stirring time for the preconcentration of Tl(I) at pH 7.0 using 0.15 g of IIP shows that 35 min is enough.

In this condition, the optimum elution time and eluent volume were 15 min and 5 mL, respectively. The concentration of eluent (nitric acid) is also important for the performance of the solid-phase preconcentration system. The effect of nitric acid concentration was studied in range of 0.0001–2.0 mol/L. The results show that the highest extraction was obtained in the concentration range of 0.01 to 2.0 mol/L. At concentrations less than 0.01 mol/L of nitric acid, the elution process

Table 1: Optimum condition for various parameters on uptake of thallium with IIP.

Parameter	Range	Optimum conditions
pH	4.0-8.0	7.0
Weight of IIP (g)	0.02-0.2	0.15
Preconcentration time (Min)	10-40	35
Elution time (Min)	5-20	15
Concentration of eluent(M)	0.0001-2.0	0.01
eluent volume(mL)	2-10	5
Aqueous phase volume (mL)	50-1000	500

was incomplete. Therefore, a 1.0 mol/L nitric acid was selected for further experiments. The change of the aqueous phase volume from 50 to 500 mL did not affect the adsorption efficiency of Tl(I). Higher volumes resulted in decrease of adsorption efficiency.

Adsorption capacity

The adsorption capacity is an important factor to evaluate the IIPs. In order to investigate the adsorption capacity of thallium on imprinted and non-imprinted polymer particles, 150 mg of polymer particles was introduced into a saturated solution of Tl(I) under the optimum conditions. The adsorption capacity of the imprinted and non-imprinted sorbent was calculated to be 9.1 and 4.9 mg /g, respectively.

Interference effects

In order to examine the effects of common coexisting ions on the extraction of Tl(I), different metals cations were added individually to the sample solution containing 10 ng/mL of analyte. Interfering species (Na^+ , K^+ , Ca^{2+}) at 1000- fold ,species (Mg^{2+} , Fe^{3+} , Cu^{2+} , Zn^{2+}) 500-fold and Tl^{3+} at 100-fold excess were added to Tl(I) solution and the extraction procedure was followed. The results of interference effects are shown in Table 2. Some of the interfered metal ions could be masked, using appropriate masking agents such as EDTA, that explained and used in our previously article [28].

These ions were chosen because they coexist with thallium ions in natural sources and also have more or less the same charge or ionic radius with Tl(I) ion. It can be noticed that the presence of majority of cations has no obvious influence on the adsorption of thallium ions under the selected conditions. This shows that

the proposed method is suitable for the determination of Tl(I) in real samples

Statistical and calibration parameters

Under the optimum conditions (Table 1), the calibration curve was linear over the concentration range of 2.5-300 ng /mL thallium(I) ions. The linear regression equation for thallium was $A = 0.0078C_{\text{Tl}} + 0.0056$ ($R^2 = 0.998$).

Five replicate determinations of 50 ng/ mL thallium solutions resulted a relative standard deviation of 3.5%. The limit of detection corresponding to three times of the standard deviation of blank was found to be 0.1ng/ mL.

Real sample Analysis

To assess the applicability of the procedure for real samples, it was applied for extraction and determination of thallium ions in water samples (tap water and well water). The results are summarized in Table 3. The reliability of the method was verified by the analysis of the samples spiked with the known amounts of thallium and good recoveries were obtained in all samples.

Comparison of Tl^+ and Tl^{3+} ion imprinted polymer

Thallium can be found in nature as Tl(I) and Tl(III) species. Thallium(I) has higher stability, than Tl(III) forms complexes of greater stabilities. The Tl(III) forms a ternary complex with DCQ and vinylpyridine (VP), while Tl(I) forms a binary complex with DCQ. According to the results, a wider pH range can be used for Tl(I) ion imprinted polymer because of its higher stability. Acetonitrile and 2-methoxyethanol solvents were used as porogen solvents in the preparation of Tl(III) ion imprinted polymer and Tl(I) ion imprinted polymer, respectively. The relevant results are shown in Table 4.

Table 2: Effect of interferences on determination of 10 ng/ mL thallium (I) in the presence of foreign ions.

Interfering ion	Relative absorbance ^a
Na ⁺	1.03
K ⁺	1.02
Ca ²⁺	1.06
Mg ²⁺	1.07
Zn ²⁺	1.04
Cu ²⁺	1.09
Fe ³⁺	1.05
Tl ³⁺	1.08

Table 3: Result of determination of thallium (I) in water samples.

Sample	Added thallium(I) (ng /mL)	Found thallium(I) (ng /mL)	RSD%	Recovery
Tap water ^a	0	ND		-
	20.0	19.0	3.0	95
	40.0	41.5	3.6	103.7
Well water ^a	0	ND		-
	10.0	9.4	4.0	94

^a Mashhad city**Table 4: Comparison of Tl⁺ and Tl³⁺ ion imprinted polymer.**

Complex	Tl ³⁺ -ion imprinted polymer ternary(Tl ³⁺ :VP:DCQ)	Tl ⁺ -ion imprinted polymer binary(Tl ⁺ :DCQ)
Stoichiometry	1:2:2	1:2
Linear range(ng /mL)	1-600	2.5-300
porogen solvent	Acetonitrile	2-methoxyethanol
adsorption capacity(mg /g)	9.6	9.1

CONCLUSIONS

In this study, a thallium (I) ion-imprinted polymer as a new sorbent has been synthesized for Tl(I) ion and also compared with Tl(III) ion imprinted polymer with different pH and stoichiometry. This sorbent was used for solid phase extraction and preconcentration of Tl(I) ions from aqueous solutions. In the present work, a DCQ-Tl(I) complex was used for preparation of the ion-imprinted sorbent. The imprinted polymer exhibits valuable characteristics for adsorption and preconcentration of the target Tl(I) ions in the aqueous solution. The optimal pH for quantitative enrichment was 7 ± 0.2 . The presence of

majority of cations has no obvious influence on the adsorption of thallium ions under the optimized conditions. The main advantages of this sorbent are: ease and simplicity of preparation of Tl(I) ion imprinted polymer for separation, preconcentration and determination of thallium(I) ions.

Acknowledgements

The authors wish to thank the Ferdowsi University of Mashhad for the financial support of this work.

Received : Jan. 1, 2019 ; Accepted : Jul. 1, 2019

REFERENCES

- [1] Fan H., Li J., Sun T., An Ion-Imprinted Amino-Functionalized Silica Gel Sorbent Prepared by Hydrothermal Assisted Surface Imprinting Technique for Selective Removal of Cadmium (II) from Aqueous Solution, *Applied Surface Science*, **258**: 3815-3822 (2012).
- [2] Fan H., Liu J., Yao H., Zhang Z., Yan F., Li W., Ionic Imprinted Silica-Supported Hybrid Sorbent with an Anchored Chelating Schiff Base for Selective Removal of Cadmium(II) Ions from Aqueous Media. *Ind. Eng. Chem. Res.*, **53**: 369- 378 (2014).
- [3] Pan J., Zou X., Li C., Liu Y., Yan Y., Han J., Synthesis and Applications of Ce(III)-Imprinted Polymer Based on Attapulgite as the Sacrificial Support Material for Selective Separation of Cerium(III) Ions, *Microchim Acta.*, **171**: 151-160 (2010).
- [4] Nishad P., Bhaskarapillai A., Velmurugan S., Narasimhan S.V., Cobalt (II) Imprinted Chitosan for Selective Removal of Cobalt During Nuclear Reactor Decontamination. *Carbohydrate Polymers*, **87**: 2690-2696 (2012).
- [5] Bayramoglu G., Yakup Arica M., Synthesis of Cr (VI)-Imprinted Poly (4-vinyl pyridine-co-hydroxyethyl methacrylate) Particles: Its Adsorption Propensity to Cr (VI), *Journal of Hazardous Materials*, **187**: 213- 221 (2011).
- [6] Zhang Z., Xu X., Yan Y., Kinetic and Thermodynamic Analysis of Selective Adsorption of Cs(I) by a Novel Surface Whisker-Supported Ion-Imprinted Polymer, *Desalination*, **263**: 97- 106 (2010).
- [7] Shamsipur M., Besharati-Seidani A., Synthesis of a Novel Nanostructured Ion-Imprinted Polymer for Very Fast and Highly Selective Recognition of Copper(II) Ions in Aqueous Media, *Reactive & Functional Polymers*, **71**: 131- 139 (2011).
- [8] To Hoai N., Yoo D., Kim D., Batch and Column Separation Characteristics of Copper-Imprinted Porous Polymer Micro-Beads Synthesized by a Direct Imprinting Method, *Journal of Hazardous Materials*, **173**: 462- 467 (2010).
- [9] Shamsipur M., Besharati-Seidani A., Fasihi J., Sharghi H., Synthesis and Characterization of Novel Ion-Imprinted Polymeric Nanoparticles for Very Fast and Highly Selective Recognition of Copper(II) Ions, *Talanta*, **83**: 674-481 (2010).
- [10] Xie F., Liu G., Wu F., Guo G., Li G., Selective Adsorption and Separation of Trace Dissolved Fe(III) from Natural Water Samples by Double Template Imprinted Sorbent with Chelating Diamines, *Chemical Engineering Journal*, **183**: 372-380 (2011).
- [11] Singh D.K., Mishra S., Synthesis and Characterization of Hg (II)-Ion-Imprinted Polymer: Kinetic and Isotherm Studies, *Desalination*, **257**: 177- 183 (2010).
- [12] Zhang Z., Li J. Song X., Maand J., Chen L., Hg²⁺ Ion-Imprinted Polymers Sorbents Based on Dithizone-Hg²⁺ Chelation for Mercury Speciation Analysis in Environmental and Biological Samples, *RSC Adv*, **4**: 46444- 46453 (2014).
- [13] Vatanpour V., Madaeni S., Zinadini S., Rajabi H., Development of Ion Imprinted Technique for Designing Nickel Ion Selective Membrane. *Journal of Membrane Science*, **373**: 36- 42 (2011).
- [14] Teixeira Tarley C., Andrade F.N., de Santana H., Augusto Morozin Zaia D., Alberto Beijo L., Gava Segatelli M., Ion-Imprinted Polyvinylimidazole-Silica Hybrid Copolymer for Selective Extraction of Pb(II): Characterization and Metal Adsorption Kinetic and Thermodynamic Studies, *Reactive & Functional Polymers*, **72**: 83-91 (2012).
- [15] Cai X., Li J., Zhang Z., Yang F., Dong R., Chen L., Novel Pb²⁺ Ion Imprinted Polymers Based on Ionic Interaction via Synergy of Dual Functional Monomers for Selective Solid-Phase Extraction of Pb²⁺ in Water Samples, *ACS Appl. Mater. Interfaces*, **6**: 305-313 (2014).
- [16] Godlewska-Z' ylkiewicz B., Les'niewska B., Wawreniuk I., Assessment of Ion Imprinted Polymers Based on Pd(II) Chelate Complexes for Preconcentration and FAAS Determination of Palladium, *Talanta*, **83**: 596-604 (2010).
- [17] Zambrzycka E., Roszko D., Leńniewska B., Wilczewska A.Z., Godlewska-Żyłkiewicz B., Studies of Ion-imprinted Polymers for Solid-Phase Extraction of Ruthenium from Environmental Samples before Its Determination by Electrothermal Atomic Absorption Spectrometry, *Spectrochimica Acta Part B*, **66**: 508-516 (2011).

- [18] Shakerian F., Dadfarnia S., Haji Shabani A., Nili Ahmad Abadi. M., Synthesis and Characterisation of Nano-Pore Antimony Imprinted Polymer and Its Use in the Extraction and Determination of Antimony in Water and Fruit Juice Samples, *Food chemistry*, **145**: 571-577 (2014).
- [19] Fan H., Tang Q., Sun J., Zhang Z., Selective Removal of Antimony(III) from Aqueous Solution Using Antimony(III)-Imprinted Organic-Inorganic Hybrid Sorbents by Combination of Surface Imprinting Technique with Sol-Gel Process, *Chemical Engineering Journal*, **258**: 146-156 (2014).
- [20] Shirvani-Arani S., Ahmadi S., Bahrami-Samani A., Ghannadi-Maragheh M., Synthesis of Nano-Pore Samarium (III)-Imprinted Polymer for Preconcentrative Separation of Samarium Ions from Other Lanthanide Ions via Solid Phase Extraction, *Analytica Chimica Acta*, **623**: 82-88 (2008).
- [21] Arbab-Zavar M., Chamsaz M., Zohuri G., Darroudi A., Synthesis and Characterization of Nano-Pore Thallium (III) Ion-Imprinted Polymer as a New Sorbent for Separation and Preconcentration of Thallium, *Journal of Hazardous Materials*, **185**: 38-43 (2011).
- [22] Darroudi A., Arbab Zavar. M., Chamsaz .M., Zohuri. G., Ashraf. N., Ion-Imprinted Polymer Mini-Column for on-Line Preconcentration of Thallium (III) and Its Determination by Flame Atomic Absorption Spectrometry, *Anal. Methods*, **4**: 3798-3803 (2012).
- [23] Ahmadi S., Noori-Kalkhoran O., Shirvani-Arani S., Synthesis and Characterization of New Ion-Imprinted polymer for Separation and Preconcentration of Uranyl (UO_2^{2+}) Ions, *Journal of Hazardous Materials*, **175**: 193-197 (2010).
- [24] Zhou L., Shang C., Liu Z., Huang G., Adesina A., Selective Adsorption of Uranium(VI) from Aqueous Solutions Using the Ion-Imprinted, Magnetic Chitosan Resins, *Journal of Colloid and Interface Science*, **366**: 165-172 (2012).
- [25] Sadeghi S., Sheikhzadeh E., Solid Phase Extraction Using Silica Gel Modified with Murexide for Preconcentration of Uranium (VI) Ions from Water Samples, *Journal of Hazardous Materials*, **163**: 861-868 (2009).
- [26] Shakerian F., Dadfarnia S., Haji Shabani A., Synthesis and Application of Nano-Pore Size Ion Imprinted Polymer for Solid Phase Extraction and Determination of Zinc in Different Matrices, *Food Chemistry*, **134**: 488- 493 (2012).
- [27] Leonard A., Gerber G.B., Mutagenicity; Carcinogenicity and Teratogenicity of Thallium Compounds, *Mutat. Res*, **387**: 47-53 (1997).
- [28] Chamsaz M., Arbab-Zavar M., Darroudi A., Salehi T., Preconcentration of Thallium(I) by Single Drop Microextraction with Electrothermal Atomic Absorption Spectroscopy Detection using Dicyclohexano-18-crown-6 as Extractant System, *Journal of Hazardous Materials*, **167**: 597- 601 (2009).