

Synthesis, characterization, and application of novel Zn(II)-ionic imprinted polymer for preconcentration of Zn(II) ions from aqueous solution

T Wirawan^{1,2*}, G Supriyanto^{2,3}, A Soegianto⁴

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Mulawarman, Samarinda, Indonesia

²Department of Chemistry, Faculty of Science and Technology, University of Airlangga, Surabaya, Indonesia

³Laboratory of Sensor and Biosensor, Institute of Tropical Diseases, University of Airlangga, Surabaya, Indonesia

⁴Department of Biology, Faculty of Science and Technology, University of Airlangga, Surabaya, Indonesia

*Corresponding author: twirawan@yahoo.co.id

Abstract. Preparation of a new Zn²⁺ ion-imprinted polymer (Zn-IIP) is presented in this report. The Zn-IIP are prepared by precipitation polymerization using 8-hydroxyquinoline (8HQ) as a ligand, methacrylic acid (MAA) as functional monomer, and ethylene glycol dimethacrylate (EGDMA) as a cross-linker has been prepared. The benzoyl peroxide and ethanol/acetonitrile (2:1) mixture were used as initiator and porogen, respectively. Precipitation polymerization was carried out by heating in a water bath at 60°C for 8 hours. After polymerization, cavities in the polymer particles corresponding to the Zn²⁺ ions were created by leaching the polymer with 2 mol L⁻¹ HNO₃. The polymer was washed with aquabidest and dried in an oven at the temperature of 60°C for 24 hours. The Zn-IIP was characterized by Fourier Transform Infrared Spectrophotometry (FT-IR) and Scanning Electron Microscopy (SEM). The synthesized Zn-IIP was used as a new adsorbent for solid phase extraction (SPE) of Zn(II) prior to Flame Atomic Absorption Spectrometry (FAAS) determination. The experimental parameters for SPE, such as pH of the sample, loading rate, and elution volume, have been optimized. The effect of pH of the sample on the extraction of analyte was studied in batch mode. The effects of loading rate and elution volume on the extraction of analyte were studied in dynamic mode by loading of the sample through IIP-SPE cartridge containing 100 mg of the synthesized Zn-IIP. The imprinted polymer (Zn-IIP) have bands at 3433.06 cm⁻¹ (O-H), 1508.23 cm⁻¹ (C=N aromatics), 1284.5 cm⁻¹ (C-N aromatics), 1056.9 cm⁻¹ (C-O phenol), 1724.24 cm⁻¹ (C=O), and 1639.38 cm⁻¹ (conjugated C=O with C=C). The Scanning Electron Microscopy (SEM) images of IIP and NIP show that the IIP is seen to have more cavities than NIP. The optimum pH for quantitative Zn(II) retention was 5.5, and the elution was completed with 2 mL of 1.0 mol L⁻¹ nitric acid. The optimum loading rate was 0.5 mL min⁻¹. The recovery of Zn(II) from solution samples after its SPE extraction on IIP with 50-fold theoretical preconcentration was 94.60-104.50%. The LOD and LOQ with 50-fold theoretical preconcentration obtained were 0.0073 mg L⁻¹ and 0.0244 mg L⁻¹, respectively.



1. Introduction

Zinc is one of the most important essential trace elements in human nutrition, the second most abundant transition metal in the body, and highest concentrations occur in the brain [1]. Zinc deficiency in the human body causes several disorders including growth retardation, diarrhea, eye and skin lesions, immunity depression, and malfunction of wound healing. On the other hand, excessive zinc intake also causes various acute and chronic adverse effects [2,3]. Zinc is used extensively in several industries, such as mining, metal coating, and battery production. Zinc is also found in industrial paints, ceramics, wood, fabrics, drugs, sun blocks, and deodorants [4].

Several analytical techniques including spectrophotometry [5], spectrofluorometry [6], voltammetry [7], optical sensor [8], electrochemical sensors [9], flame atomic absorption spectrometry [10], electrothermal atomic absorption spectrometry [11], and inductively coupled plasma optical emission spectrometry [12] have been used for the direct determination of zinc in different matrixes. Most of these methods suffer from chemical interferences, poor limits of detection, competition effects, disturbance of solution equilibrium, long equilibrium time, or poor preconcentration and poor selectivity [13]. In an effort to improve sensitivity, several methods such as preconcentration techniques have been developed. Several procedures, such as liquid–liquid extraction [14], cloud point extraction [15,16], co-precipitation [17,18], and solid phase extraction, have been proposed and applied for the enrichment and separation of zinc.

In recent years, SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples. Solid phase extraction has proven to be a fast and inexpensive technique for the determination of trace metals with a use of low sample volumes. High preconcentration factor and low sample volume requirements were major advantages of the technique [19]. Solid phase extraction (SPE) is a sensitive, inexpensive, and fast sample preparation process that involves partitioning between a liquid phase. The analytes were separated from the solution by sorption on the solid sorbent according to their physical and chemical properties [20].

The solid phase extraction method is an alternative to replace solvent extraction. Solid phase extraction is a chromatographic sample preparation technique that is used for the separation, purification, and preconcentration of chemical compounds from solution [21]. In SPE, the sample is detained or adsorbed and later eluted adsorbent with elution in one stage or gradient. There are several advantages compared to solvent extraction, including reducing the use of hazardous solvents, requires a shorter time, do automation [22], facilitate storage and transport [23], the component desired can be taken out by using a selective solvent [24], and can be used for the separation and purification [25]. One of the most promising groups of new sorbents is an ionic-imprinted polymer (IIP). The ion-imprinting idea is based on the formation of a complex of given metal ion (serving as a template) with appropriate ligand and its subsequent immobilization in a cross-linked polymeric matrix. Upon metal ion extraction from the polymetric body spatially pre arranged binding sites are left in the sorbent structure. Therefore, due to their predetermined selectivity thus obtained synthetic materials are able to recognize and preferentially bind the metal ion which was used as a template in the polymerization process which offers new possibilities in separation science [26].

Recently, IIP has been growing rapidly as an adsorbent for SPE because it has the advantage on the enrichment factor and high selectivity. Applications of IIP as adsorbent in the SPE has been widely reported in the extraction of arsenic [27], iron [28,29], cadmium [30,31], mercury [32], copper [33], lead [34,35], and zinc [36-38].

In the preparation of IIP, suitable ligand groups were brought into contact with metal ions to form a complex that was then covered with a crosslinked polymer. After removal of the template (metal ion), the uptake of metal ions is strongly enhanced in many cases and also more selective. The selectivity of IIP mainly because of the following factors [39]: i) the specificity of interaction of ligand with the metal ion, ii) the coordination geometry and the coordination number of metal ion, iii) the charge of the metal ion, and iv) to a large extent on the size of the metal ion.

In this paper, we report the synthesis, characterization, and application of Zn-IIP for zinc preconcentration by SPE. Zinc concentration was analyzed using Flame Atomic Absorption Spectrophotometer (FAAS). The IIP was synthesized using 8-hydroxyquinoline (8HQ) as complexing ligands, methacrylic acid (MAA) as the functional monomer and ethylene glycol dimethacrylate (EGDMA) as agents of cross-linking. Characterization of the IIP was investigated using Fourier Transform Infrared Spectrophotometry (FTIR) and Scanning Electron Microscopy (SEM). The experiment parameter such as pH of the solution, flow rate, volume of HNO_3 for elution was investigated. This method was applied for the enrichment of trace amount of zinc(II) ion from aqueous solutions..

2. Experiment section

2.1. Materials

The materials used were: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, Germany), HNO_3 (Merck, Germany), 8-hydroxyquinoline (8HQ) (Sigma Aldrich, US), methacrylic acid (MAA) (Sigma Aldrich, US), ethylene glycol dimethacrylate (EGDMA) (Sigma Aldrich, US), benzoyl peroxide (Merck, Germany), ethanol (Merck, Germany), and acetonitrile (Merck, Germany).

2.2. Instrumentation

The characteristic of functional groups among adsorbent was confirmed by Fourier Transform Infrared Spectrophotometer (Perkin Elmer Frountier-89485), The surface morphological image of adsorbent was obtained by Scanning Electron Microscopy (FEL, Inspect-S50). The concentration of zinc was analyzed using an atomic absorption spectrophotometer (Perkin Elmer, AA 700). A pH-meter (Mettler Toledo) was used for the pH measurements.

2.3. Procedure

2.3.1. Preparation of IIP

The ionic imprinted polymer was synthesized following the method proposed by Barciela-Alonso *et al.* [40]. Therefore, 0.0287 g (0.1 mmol) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.0363 g (0.25 mmol) 8-hydroxyquinoline were mixed in 60 mL of porogen (2:1 ethanol-acetonitrile). This solution was stirred for 30 min with a magnetic stirrer. Finally, 0.34 mL (4 mmol) of methacrylic acid (monomer), 0.0485 g (0.2 mmol) of benzoyl peroxide (initiator), and 3.77 mL (20 mmol) of ethylene glycol dimethacrylate (cross-linker) were added, the glass tube was purged with nitrogen for 5 min and immediately sealed. Precipitation polymerization was carried out by heating in a water bath at 60°C for 8 hours while stirring with a magnetic stirrer. The polymer obtained was filtered, washed with ethanol, and oven-dried for 2 hours at 60°C . The imprinted zinc ions were leached from the polymer by using 100 mL of 1 mol L^{-1} HNO_3 solution in magnetic stirrer for 30 min. The adsorbent was washed with distilled water, filtered, and dried at 100°C for 24 hours. The same procedure, except the presence of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and leaching, was applied for preparing non-imprinted polymers (NIP). The polymer was prepared by the same procedure, except the presence of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 8-hydroxyquinoline, and leaching. Ionic imprinted polymer and non-ionic imprinted polymer were characterized by FTIR and SEM.

2.3.2. Effect of pH

The effect of pH solution was tested by shaking 0.01 g IIP and 20 mL of the Zn(II) solution (4.5 mg L^{-1}) at various pH for 10 min. The pH of the sample solutions was varied from pH 4 to 8. The IIP was separated by filtration and concentration of Zn(II) in the filtrate was determined by FAAS.

2.3.3. Effect of eluent volume

A cartridge with an i.d. of 5 mm was filled with 0.1 g of dry IIP. 50 mL of 2.5 mg L^{-1} Zn(II) solution, adjusted to pH 5.5, was passed through the cartridge. Then the solution of 1 mol L^{-1} HNO_3 was passed to desorb Zn(II) from the cartridge. The concentration of Zn(II) was determined by FAAS. The volume of HNO_3 was varied from 0.5 to 5.0 mL.

2.3.4. Effect of flow rate

A cartridge with an i.d. of 5 mm was filled with 0.1 g of IIP. 50 mL of 2.5 mg L⁻¹ Zn(II) solution, adjusted to pH 5.5, was passed through the column at various of flow rate. The flow rate was varied from 0.2 to 2.2 mL min⁻¹. Then, Zn(II) was eluted from the cartridge with 2 mL of 1 mol L⁻¹ HNO₃ and measured by FAAS.

2.3.5. Solid phase extraction

A cartridge with an i.d. of 5 mm was filled with 0.1 g of dry ionic-imprinted polymers. The sorbents were conditioned by passing 3 mL of buffer pH 5.5. For the loading of the analyte, Zn(II) standard solution was adjusted to pH 5.5 and passed through the cartridge at a flow rate of 0.5 mL min⁻¹. Then, Zn(II) was eluted from the cartridge with 2 mL of 1 mol L⁻¹ HNO₃ measured by FAAS.

3. Result and discussion

The new ionic imprinting material was prepared by using 8-hydroxyquinoline (8HQ) as complexing ligands, methacrylic acid (MAA) as the monomer, and ethylene glycol dimethacrylate (EGDMA) as agents of cross-linking. The polymer was synthesized by precipitation polymerization technique. The synthesis of IIP was carried out in three step (Figure 1): (1) The complexation Zn(II) with 8HQ, (2) the polymerization of monomer in the presence of the template, and (3) the removal of the template after copolymerization from the polymer.

3.1. Characterization of IIP

The FTIR spectra of complexing ligand (8HQ), monomer (MAA), crosslinker (EGDMA), polymer, and IIP are presented in Figure 2. The spectra of 8HQ (Figure 2e) has a characteristic peaks at 3433.06 cm⁻¹ (O-H), 1508.23 cm⁻¹ (C=N aromatics), 1284.5 cm⁻¹ (C-N aromatics) and 1056.9 cm⁻¹ (C-O phenol). The spectra of MAA (Figure 2d) has a characteristic peaks of 1527.52 cm⁻¹ (C=C), 1473.51 cm⁻¹ (C=C aromatic), 1203.5 cm⁻¹ (C-O), and 1693.38 cm⁻¹ (conjugated C=O with C=C). The spectra of EGDMA (Figure 2c) has characteristic peaks at 1245.93 cm⁻¹ (C-O), 1724.24 cm⁻¹ (C=O), and 1639.38 cm⁻¹ (conjugated C=O with C=C). The polymer formed by the addition of the C=C double bond into a single C-C bond, shown in the FTIR spectra of polymers (Figure 2b) that are absence peak at 1527.52 cm⁻¹ (C=C) when compared to spectra of MAA. The IIP formed indicated by the appearance of a peak at 1492.8 cm⁻¹ (C=C aromatic) of IIP spectra (Figure 2a) compared with the spectra of polymers.

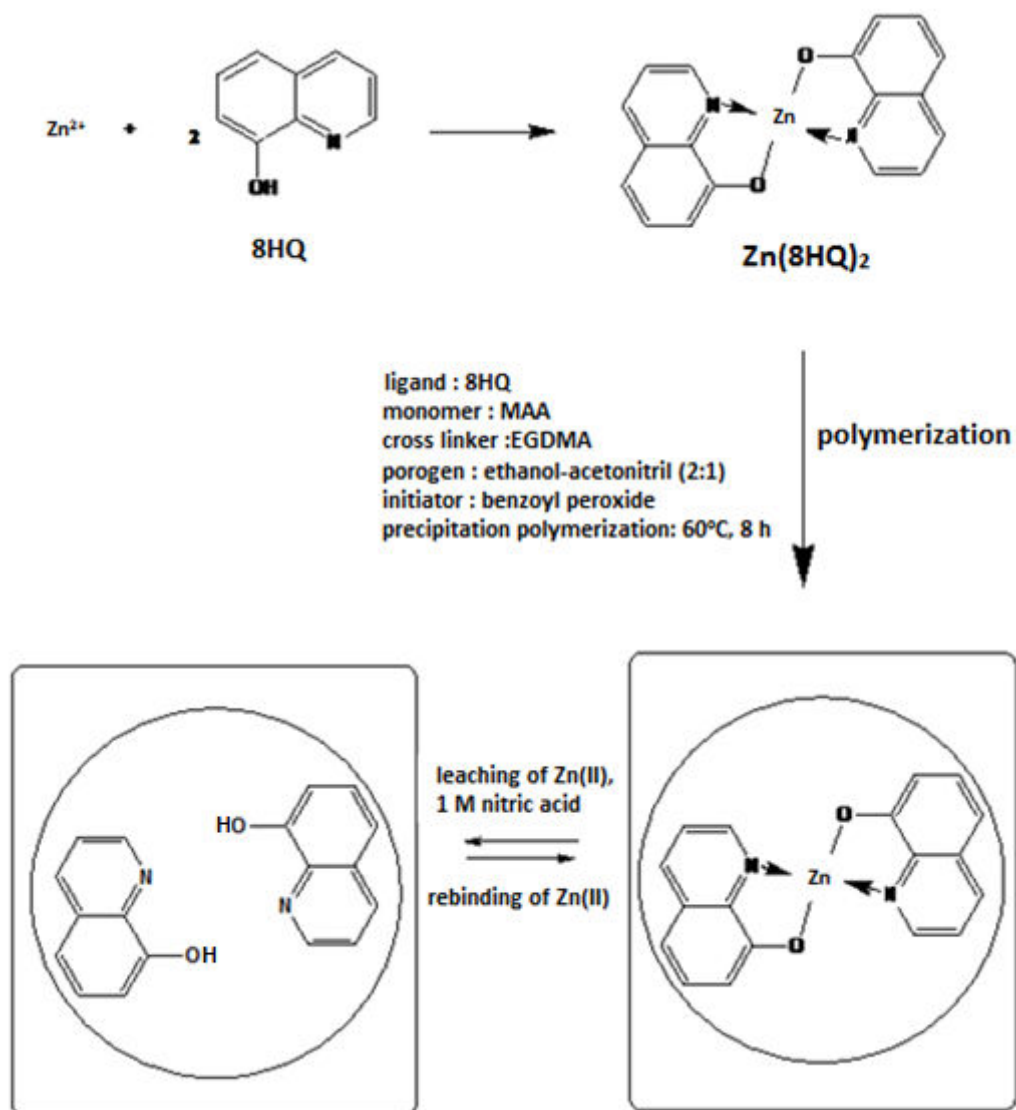


Figure 1. Illustration of IIP formation

Scanning electron microscopy (SEM) images are presented in Figure 3. There are obvious differences between the scanning micrograph of NIP and IIP. The textural characteristics were closely examined at 20k x magnification. The particles of both NIP and IIP were present a spherical shape. It should be spherical shape when IIP was synthesized by precipitation polymerization. The IIP is seen to have more cavities than NIP, this is because Zn in IIP has been eluted.

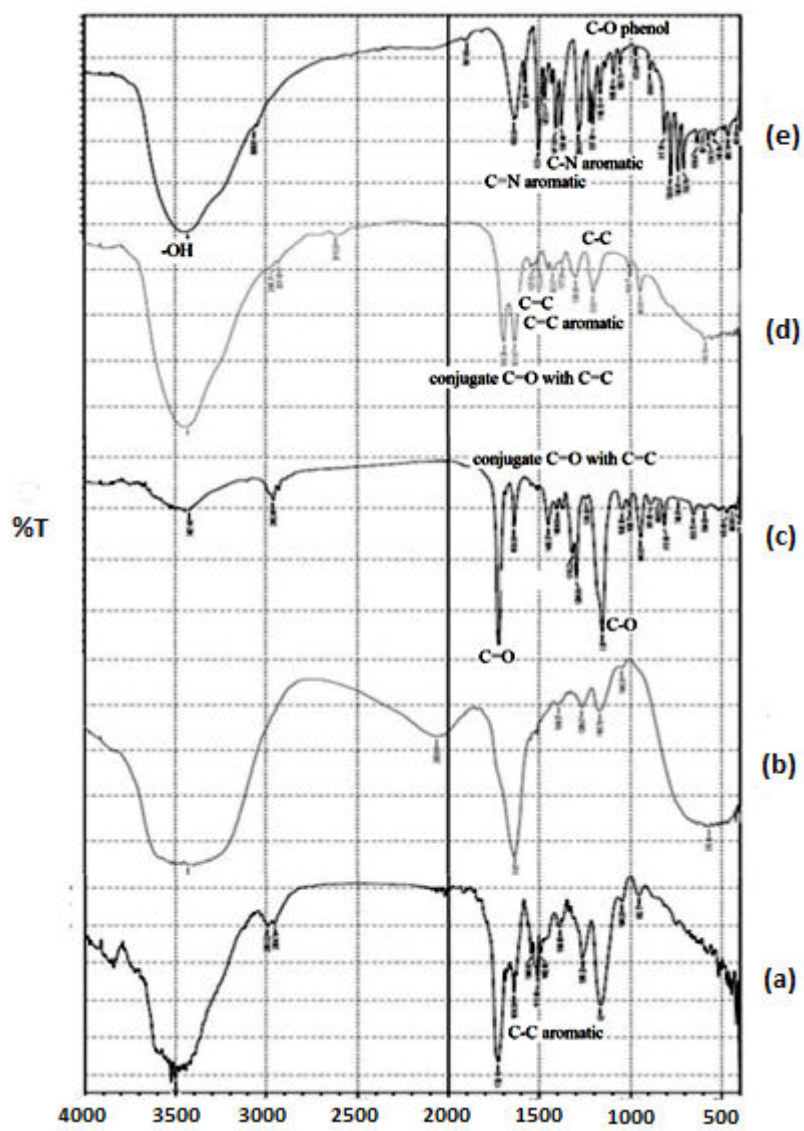
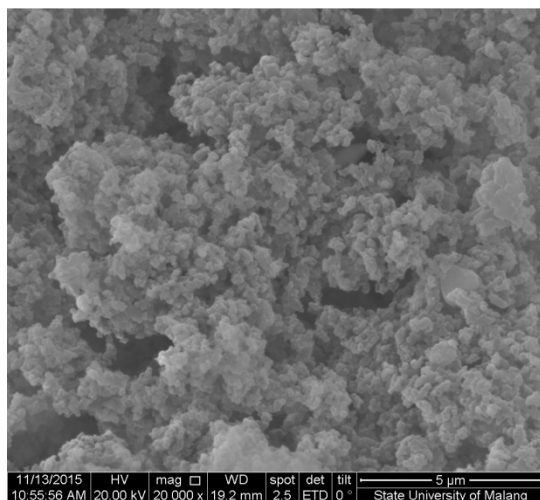
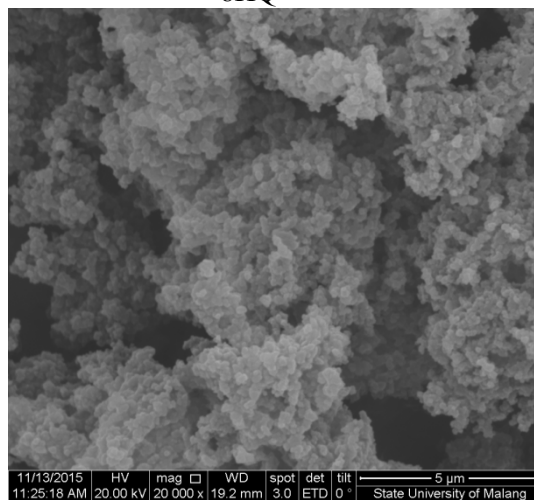


Figure 2. FTIR spectra of (a) IIP, (b) polymer, (c) EGDMA, (d) MAA, and (e) 8HQ



a



b

Figure 3. SEM images of (a) NIP and (b) IIP

3.2. Influence of initial pH on Zn(II) adsorption

Among all other parameters, pH of solution has been found to be the most important one. It not only influences the speciation of metal ions but also the ionization of surface functional groups of adsorbent [41]. The influence of the initial pH on adsorption of Zn(II) on the IIP was studied to determine the optimum pH. The adsorption of Zn(II) as a function of the pH is shown in Figure 4. The adsorption of Zn(II) increased greatly between pH 4.5 to 5.5 and then gradually decreased. In a highly acidic environment, several functional groups become protonated and act as positively charged species, resulting in reduced attraction between the metals and the minerals [4,42]. With increasing pH, electrostatic repulsion decreases due to a reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption [43]. At higher pH values OH⁻ ions compete for Zn(II) with the active sites on the surface of the adsorbents [44]. However, at an alkaline environment, the solubility of metals decreases allowing precipitation, which may complicate the sorption process. Zn(II) ions react with OH⁻ ligand to precipitate to Zn(OH)₂.

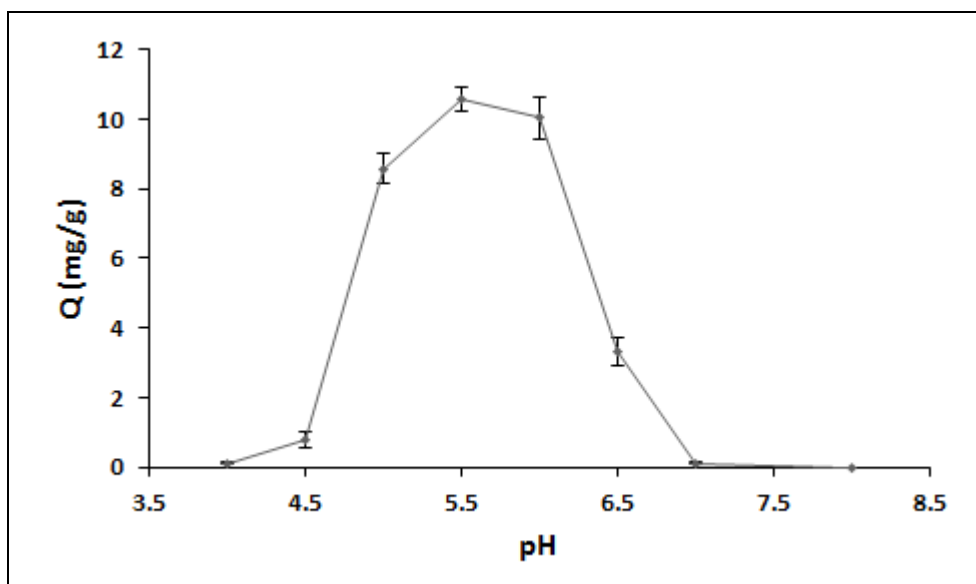


Figure 4.
Influence of
pH on the
adsorption of
Zn(II) on IIP

3.3. Influence of eluent volume

The influence of the eluent volume on adsorption of Zn(II) on the IIP was studied. After sample loading, the adsorbed Zn(II) were eluted by passing 1 mol L⁻¹ HNO₃ at different volume (from 0.5 to 5 mL) and the result was presented in Figure 5. The eluted of Zn(II) was increased greatly from 0.5 to 1.5 mL and then increased slightly from 1.5 to 2 mL. The volume above of 2 mL was constant and volume 2 mL was chosen as optimum volume. This result was similar to the result obtained by Ebrahimzadeh *et al.* [45], increasing in volume and concentration of eluent volume caused higher recovery. The eluting solution must be correctly chosen to ensure stronger affinity of the trace element for the solvent, to ensure disruption of its interaction with the sorbent [19].

3.4. Influence flow rate

In set sorption time applying high sample flow rate may seem favorable in terms of obtaining high enrichment factor due to higher sample volume loaded onto the column. However, sorption effectiveness is limited by the sorption kinetics, may be deteriorated [26]. The sample flow-rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration [19]. Different experiments were performed in order to find the optimum flow rates for the Zn(II) standard solution loading. The solution of Zn(II) standard was passed at a different flow rate

(from 0.2 to 2.25 mL min⁻¹). As shown in Figure 6, concentration of Zn(II) decrease for flow rates larger than 0.5 mL min⁻¹. In order to decrease the time needed for analysis, the optimum flow rate was chosen as 0.5 mL min⁻¹.

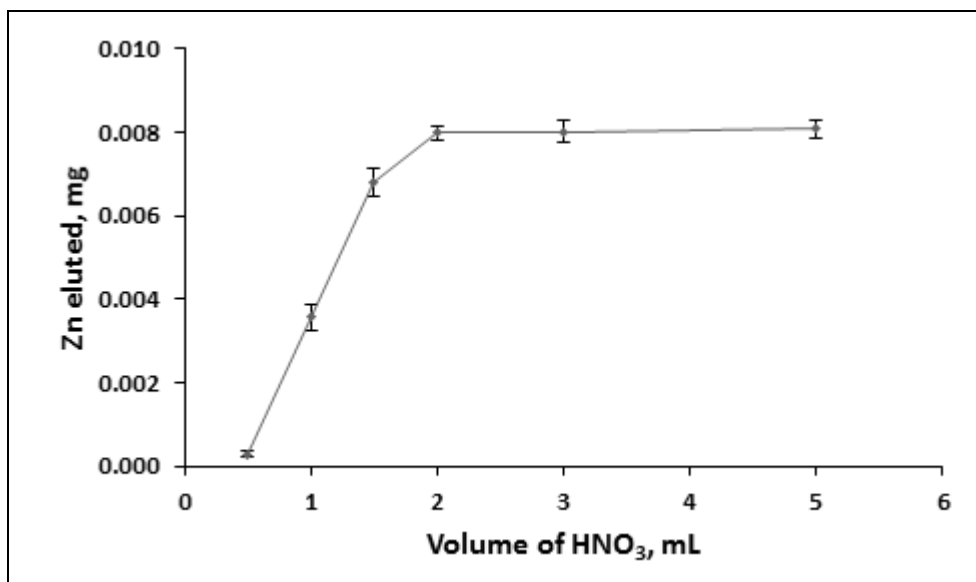


Figure 5.
Influence of
eluent volume
on the
elution of
Zn(II) on IIP

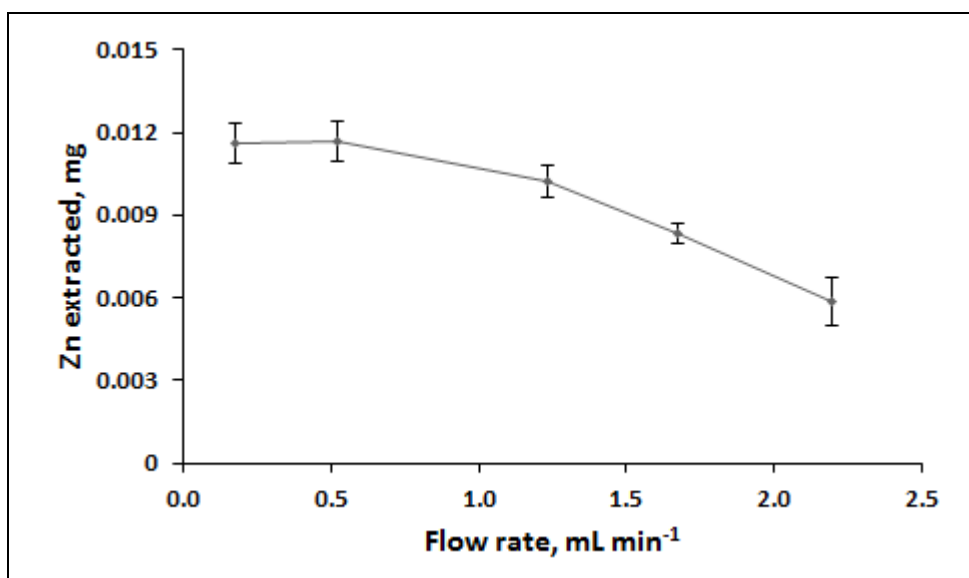


Figure 6.
Influence of
eluent flow
rate on the
extraction of
Zn(II) on IIP.

3.5. Analytical characterization

The limit of detection (LOD) and limit of quantification (LOQ) were calculated according to $LOD = (3SD)/m$ and $LOQ = (10SD)/m$, where SD is the standard deviation and m is the slope of the calibration graph (Figure 7 and Figure 8). The LOD and LOQ obtained were 0.3157 mg L⁻¹ and 1.0523 mg L⁻¹ for without preconcentration, and 0.0073 mg L⁻¹ and 0.024 mg L⁻¹ for with 50-fold theoretical preconcentration.

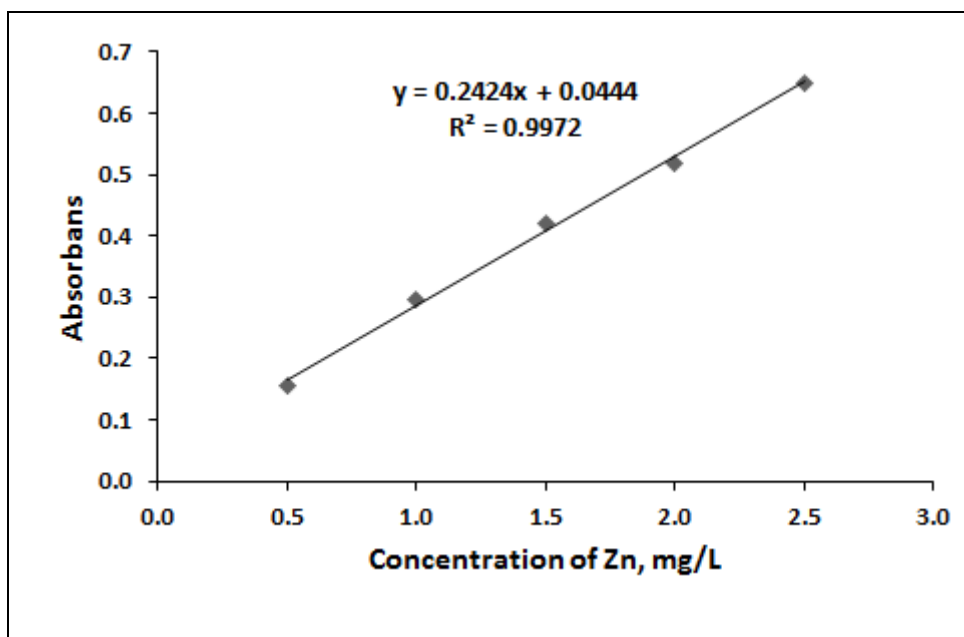


Figure 7.
Calibration graph
of Zn solution
without
preconcentration

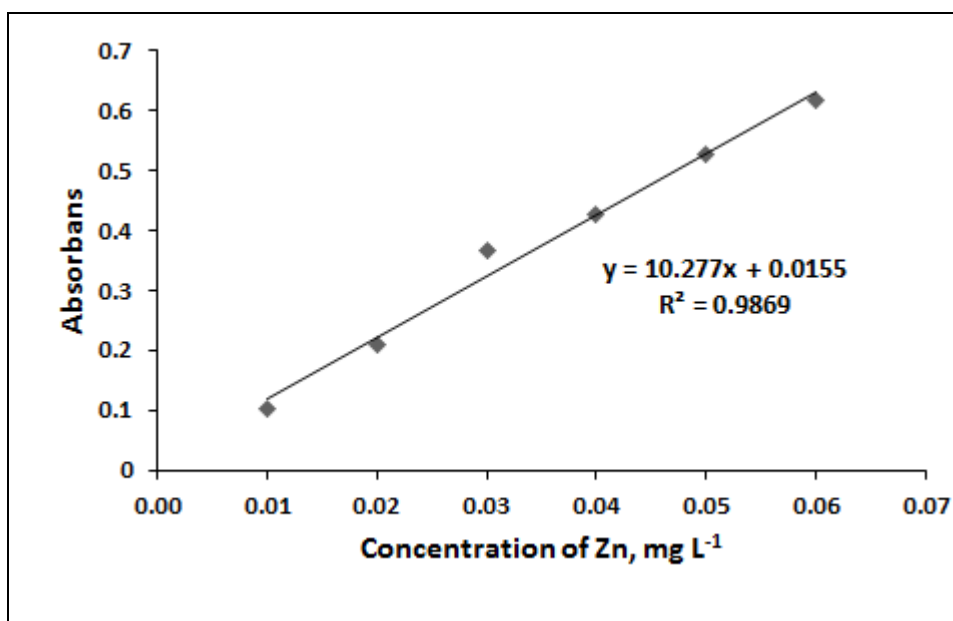


Figure 8.
Calibration
graph of Zn
solution with
50-fold
theoretical
preconcentration
.

The synthesized IIP was then applied as an adsorbent for the analysis of zinc(II) by SPE-AAS (Table 1). Analytical recovery was assessed by analyzing five of zinc standard solutions 0.01-0.05 mg L⁻¹ and preconcentration by SPE. The analytical recovery obtained was 94.60-104.50%.

Table 1. Recovery of Zn(II) from solution samples after its SPE extraction on IIP (sample: pH: 5.5; flow rate: 0.5 mL min⁻¹; elution: 2 mL of 1 mol L⁻¹ HNO₃)

No.	Added Zn (mg L ⁻¹)	Found Zn (mg L ⁻¹)	Recovery (%)
1	0.01	0.00950	95.00
2	0.02	0.01964	98.20
3	0.03	0.02838	94.60
4	0.04	0.04180	104.50
5	0.05	0.05012	100.24
Average			98.51
SD			4.0798

The comparison of pH, load flow rate, and detection limit in the present work with those reported in the literature are given in Table 2. Generally, the detection limit obtained by this work is comparable to those of reported or better than them.

Table 2. Comparison of the proposed method with some methods reported in literature.

Sample	Adsorben	Detection	pH load flow rate eluen	LOD	References
Cr, Cu, Ni, Pb, Zn	Silica gel-bound amines phase modified with p- dimethylamino- benzaldehyde (p- DMABD)	ICP-OES	4 1.5 mL min ⁻¹ 2.0 mL of 0.5 M HCl	6.5 µg L ⁻¹	[46]
Cu, Ni, Zn	Multiwalled carbon nanotubes (MWCNTs) impregnated with di-(2- ethyl hexyl phosphoric acid) (D ₂ EHPA) and tri- n-octyl phosphine oxide (TOPO)	FAAS	5 2 mL min ⁻¹ 10 mL of 2 1 mol L ⁻¹ HNO ₃	50 µg L ⁻¹	[47]
Fe, Zn	Multiwalled carbon nanotubes (MWCNTs)	HR-CS GFAAS	9 1 mL.min ⁻¹ 1 mL of 1 mol L ⁻¹ HNO ₃	0.5 µg L ⁻¹	[48]
Ag, Cd, Cu, Zn	magnetic nanoparticles (MNPs) coated by 3- (trimethoxysilyl)-1- propanthiol and modified with 2-amino-5-mercapto- 1,3,4-thiadiazole	ICP-OES	6 - 1 mL of 1 mol L ⁻¹ HCl and 4% (w/v) thiourea	0.11 µg L ⁻¹	[49]
Zn	IIP was synthesized by using morin, 4-vinyl- pyridine (VP), ethylene- glycol dimethacrylate (EDMA) and 2,20-	ICP-OES	4 - 10 mL of 1:1 (v/v) mixture of CH ₂ Cl ₂ - DMSO	2.9 µg.L ⁻¹	[50]

Sample	Adsorben	Detection	pH load flow rate eluen	LOD	References
Zn	azobisisobutyronitrile (AIBN). IIP was prepared via precipitation polymerization using 8-hydroxyquinoline (8HQ) as a ligand, methacrylic acid (MAA) as funtional monomer, and ethylene-glycol dimethacrylate (EGDMA) as a cross-linker	FAAS	5.5 0.5 mL min ⁻¹ 2 mL of 1 mol L ⁻¹ HNO ₃	7.3 µg.L ⁻¹	Present method

4. Conclusion

Adsorbent IIP-ionic imprinted polymer (Zn-IIP) can be synthesized through a precipitation polymerization process using 8-hydroxyquinoline as a complexing ligand, methacrylic acid as a monomer and ethylene glycol dimethacrylate as a cross-linker. Ethanol-acetonitrile (2:1) and benzoyl peroxide were used as a porogen and an initiator, respectively. IIP adsorbent can be used as an adsorbent for the analysis of zinc(II) by SPE-FAAS. The optimum conditions for the SPE process were at pH 5.5 and the volume of 1 mol L⁻¹ HNO₃ solution required to elute was 2 mL. The accuracy of the method of SPE-FAAS was 94.60-104.50%. The LOD and LOQ with 50-fold theoretical preconcentration obtained were 0.0073 mg L⁻¹ and 0.0244 mg L⁻¹, respectively.

References

- [1] Que EL, Domaille DW and Chang CJ 2008 Metals in Neurobiology: Probing Their Chemistry and Biology with Molecular Imaging *Chem. Rev.* **108** 1517–49
- [2] Scherz H and Kirchoff E 2006 Trace elements in foods: Zinc contents of raw foods: comparison of data originating from different geographical regions of the world *Journal of Food Composition and Analysis* **19** 420–33
- [3] Zhao J, Hana B, Zhanga Y and Wang D 2007 Synthesis of Zn(II) ion-imprinted solid-phase extraction material and its analytical application *Anal. Chim. Acta.* **603** 87–92
- [4] Malamis S and Katsou E 2013 A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: Examination of process parameters kinetics and isotherms *J. Hazard. Mater.* **252**, 428–61
- [5] Sabel CE, Neureuther JM and Siemann S 2010 A spectrophotometric method for the determination of zinc, copper, and cobalt ions in metalloproteins using Zincon *Analytical Biochemistry* **397** 218–26
- [6] Prat MD, Guiteras J, Campano R and Beltran JE 1991 Spectrofluorimetry method for simultaneous determination of zinc and cadmium, *Journal of Fluorescence* **1(4)** 267-72
- [7] Pinto L and Lemos SG 2013 Multivariate optimization of the voltammetric determination of Cd, Cu, Pb and Zn at bismuth film. Application to analysis of biodiesel, *Microchemical Journal* **110** 417–24
- [8] Abbasitabar F, Zare-Shahabadi V, Shamsipur M and Akhon M 2011 Development of an optical sensor for determination of zinc by application of PC-ANN *Sensors and Actuators B* **156** 181–6
- [9] Singh P, Singh AK and Jain AK 2011 Electrochemical sensors for the determination of Zn²⁺ ions

- based on pendant armed macrocyclic ligand *Electrochimica Acta* **56** 5386–95
- [10] Ramakrishna TV, Robinson JW and West PW 1967 Determination of copper, cadmium, and zinc by atomic absorption spectroscopy *Anal. Chim. Acta* **37**, 20-6
- [11] Török P and Žemberyová M 2011 A study of the direct determination of Cd, Cr, Cu, Pb and Zn in certified reference, materials of soils by solid sampling electrothermal atomic absorption spectrometry *Spectrochimica Acta Part B* **66** 93–7
- [12] Souza AL, Lemos SG and Oliveira PV 2011 A method for Ca, Fe, Ga, Na, Si and Zn determination in alumina by inductively coupled plasma optical emission spectrometry after aluminum precipitation *Spectrochimica Acta Part B* **66** 383–8
- [13] Fan HT, Li J, Li ZC and Sun T 2012 An ion-imprinted amoni-functionalized silica gel sorbent prepared by hydrothermal assisted surface imprinting technique for selective removal of cadmium(II) from aqueous solution *Applied Surface Science* **258** 3815-22
- [14] Silvestre CIC, Santos JLM, Lima JLFC and Zagatto EAG 2009 Liquid–liquid extraction in flow analysis: A critical review *Anal. Chim. Acta* **652** 54–65
- [15] Tabrizi AB 2007 Cloud point extraction and spectrofluorimetric determination of aluminium and zinc in foodstuffs and water samples *Food Chemistry* **100** 1698–1703
- [16] Silva EL, Roldan PS and Giné MF 2009 Simultaneous preconcentration of copper, zinc, cadmium, and nickel in water samples by cloud point extraction using 4-(2-pyridylazo)-resorcinol and their determination by inductively coupled plasma optic emission spectrometry *J. Hazard. Mat.* **171** 1133–8
- [17] Uluozlu OD, Tuzen M, Mendil D and Soylak M 2010 Coprecipitation of trace elements with Ni^{2+} /2-Nitroso-1-naphthol-4-sulfonic acid and their determination by flame atomic absorption spectrometry *J. Hazard. Mat.* **176** 1032–7
- [18] Feist B and Mikula B 2014 Preconcentration of some metal ions with lanthanum-8-hydroxyquinoline co-precipitation system *Food Chemistry* **147** 225–9
- [19] Camel V 2003 Solid phase extraction of trace elements *Spectrochimica Acta Part B* **58** 1177–233
- [20] Ca'mara-Martos F and Moreno-Rojas R 2016 Zinc: Properties and Determination *Encyclopedia of Food and Health* Elsevier
- [21] Wells MJM, Renner DD and Wells-Knecy C W 1994 Development and optimization of a solid phase extraction scheme for determination of the pesticide metribuzin, atrazine, metalochlor, and esfenvalerate in agricultural run off water *J. Chromatogr. A* **659** 337-48
- [22] Johnson WE, Fendinger NJ and Plimmer JR 1991 Solid phase extraction of pesticide from water: possible interferences from dissolved organic material *Anal. Chem* **63** 1510-3
- [23] Hennion MC and Coquart V 1993 Comparison of reversed-phase extraction sorbents for on-line trace enrichment of polar organic compounds in environmental aqueous samples *J. Chromatogr. A* **642** 211-24
- [24] Manes G F, Molto JC and Pico Y 1993 Solid phase extraction in multi residu pesticide analysis of water *J. Chromatogr. A* **642** 135-61
- [25] Snyder LR, Kirkland JJ and Glajch J L 1997 *Practical HPLC Method Development* Second edition John Wiley & Sons, Inc. New York
- [26] Gawin M, Konefał J, Trzewik B, Walas S, Tobiasz A, Mrowiec H and Witek E 2010 Preparation of a new Cd(II)-imprinted polymer and its application to determination of cadmium(II) via flow-injection-flame atomic absorption spectrometry *Talanta* **80** 1305-10
- [27] Tsoi YK, Ho YM and Leung KSY 2012 Selective recognition of arsenic by tailoring ion-imprinted polymer for ICP-MS quantification *Talanta* **89** 162-8
- [28] Özkütük EB and Karabörk M 2007 Fe^{3+} -Imprinted polymeric systems *Hacettepe J. Biol. & Chem.* **35** 195-202
- [29] Utku S, Yilmaz E, Türkmen D, Uzun L, Garipcan B, Say R and Denizli A 2008, Ion-imprinted thermosensitive polymers for Fe^{3+} removal from human plasma *Hacettepe J. Biol. & Chem.* **36** 291-304
- [30] Buhani, Narsito, Nuryono and Kunarti ES 2010 Production of metal ion imprinted polymer from

- mercapto-silica through sol-gel process as selective adsorbent of cadmium *Desalination* **251** 83-9
- [31] Singh DK and Mishra S 2009 Synthesis, characterization and removal of Cd(II) using Cd(II)-ion imprinted polymer *J. Hazard. Mater.* **164** 1547-51
- [32] Singh DK and Mishra S 2010, Synthesis and characterization of Hg(II)-Ion imprinted polymer; Kinetic and isotherm studies *Desalination* **257** 177-83
- [33] Dakova I, Karadjova I, Ivanov I, Georgieva V, Evtimora B and Georgiev G 2007 Solid phase selective separation and preconcentration of Cu(II) by Cu(II)-imprinted polymethacrylic microbeads *Anal. Chim. Acta* **584** 196-203
- [34] Zhang M, Zhang Z, Liu Y, Yang X, Luo L, Chen J and Yao S 2011 Preparation of core-shell magnetic ion-imprinted polymer for selective extraction of Pb(II) from environmental samples *Chem. Eng. J.* **178** 443-50
- [35] Liu Y, Liu Z, Gao J, Dai J, Han J, Wang Y, Xie J and Yan Y 2011 Selective adsorption behavior of Pb(II) by mesoporous silica SBA-15-supported Pb(II)-imprinted polymer based on surface molecularly imprinting technique *J. Hazard. Mater.* **186** 197-205
- [36] Shamsipur M and Besharati-Seidani A 2011 Synthesis of a novel nanostructured ion-imprinted polymer for very fast and highly selective recognition of copper(II) ions in aqueous media *React. Funct. Polym.* **71** 131-9
- [37] Kim M, Jiang Y and Kim D 2013 Zn²⁺-Imprinted porous polymer beads; synthesis, structure, and selective adsorption behavior for template ion *React. Funct. Polym.* **73** 821-7
- [38] Behbahani M, Salarian M, Bagheri A, Tabani H, Omid F and Fakhar A 2014 Synthesis, characterization and analytical application of Zn(II)-imprinted polymer as an efficient solid-phase extraction technique for trace determination of zinc ions in food samples *Journal of Food Composition and Analysis* **34** 81-89
- [39] Rao TP, Daniel S and Gladis JM 2004 Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid-phase extraction (IIP-SPE) *Trends in Analytical Chemistry* **23(1)** 28-35
- [40] Barciela-Alonso MC, Plata-García V, Rouco-López A, Moreda-Piñeiro A and Bermejo-Barrera P 2014 Ionic imprinted polymer based solid phase extraction for cadmium and lead preconcentration/determination in seafood *Microchim. J.* **114** 106-10
- [41] Lee SH, Jung CH, Chung H, Lee MY and Yang TW 1998 Removal of heavy metals from aqueous solution by apple residue *Process Biochemistry* **33** 205-11
- [42] Farooq U, Kozinski JA, Khan MA and Athar M 2010 Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature, *Bioresource Technology* **101** 5043-53
- [43] Jordao CP, Bragança R, Fernandes A, Ribeiro KL, Nascimento BS and Barros PW 2009 Zn(II) adsorption from synthetic solution and kaolin wastewater onto vermicompost *J. Hazard. Mater.* **162** 804-11
- [44] Bhattacharya AK, Mandal SN and Das SK 2006 Adsorption of Zn(II) from aqueous solution by using different adsorbents *Chem. Eng. J.* **123** 43-51
- [45] Ebrahimzadeh H, Behbahani M, Yamini Y, Adlmasab L and Asgharinezhad AK 2013 Optimization of Cu(II)-ion imprinted nanoparticles for trace monitoring of copper in water and fish samples using a Box-Behnken design *Reactive & Functional Polymers* **73** 23-9
- [46] Cui Y, Chang X, Zhu X, Luo H, Hu Z, Zou X and He Q 2007 Chemically modified silica gel with p-dimethylaminobenzaldehyde for selective solid-phase extraction and preconcentration of Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) by ICP-OES *Microchemical Journal* **87** 20-6
- [47] Vellaichamy S and Palanivelu K 2011 Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid-phase extraction onto MWCNTs impregnated with D2EHPA-TOPO mixture *J. Hazard. Mater.* **185** 1131-9
- [48] Krawczyk M, Jeszka-Skowron M and Matusiewicz H 2014 Sequential multi-element determination of iron and zinc in water samples by high-resolution continuum source graphite

- furnace atomic absorption spectrometry after column solid-phase extraction onto multiwalled carbon nanotubes *Microchemical Journal* **117** 138–43
- [49] Mashhadizadeh MH and Karami Z 2011 Solid phase extraction of trace amounts of Ag, Cd, Cu, and Zn in environmental samples using magnetic nanoparticles coated by 3-(trimethoxysilyl)-1-propanthiol and modified with 2-amino-5-mercapto-1,3,4-thiadiazole and their determination by ICP-OES *J. Hazard. Mater.* **190** 1023–29
- [50] Khajeh M, Kaykhaii M, Mirmoghaddam M and Hashemi H 2009 Separation of zinc from aqueous samples using a molecular imprinting technique *Intern. J. Environ. Anal. Chem.* **89(13)** 981–992