eProceedings Chemistry 1 (2016) 36-41

eISSN 2550-1453 http://eproceedings.chemistry.utm.my/

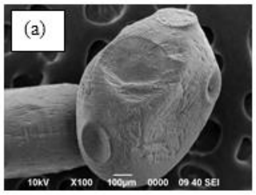
Application of magnetite-calcium alginate sorbent with flame atomic absorption spectrometry for Lead (II) ions analysis from water samples

Najwa Izzati Zainal, Faridah Mohd Marsin and Wan Aini Wan Ibrahim*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru.
Corresponding Author: wanaini@kimia.fs.utm.my

Article history :
Received September 2016
Accepted November 2016

GRAPHICAL ABSTRACT



Surface Morphology of Calcium Alginate (CaAlg) bead at 10 kV with (a) ×100 Magnification

ABSTRACT

Magnetite, Fe_3O_4 encapsulated calcium alginate (Fe_3O_4-CaAlg) was proposed as a sorbent in magnetic solid phase extraction (MSPE) of Pb(II) ions from water samples. MSPE is able to overcome the limitations of liquid-liquid extraction (LLE) and solid phase extraction (SPE). MSPE use smaller volume fraction of organic solvent for desorption compared to LLE, less tedious than LLE and SPE, and avoids channelling effect as observed in SPE. Pb(II) ions was determined using flame atomic absorption spectroscopy (FAAS) at 283.31 nm. The *as-synthesised* Fe_3O_4-CaAlg was characterized using Fourier transform infrared spectroscopy and scanning electron microscopy. Several MSPE parameters (sample volume, sample solution pH, and effect of selected co-existence ions) influencing the extraction efficiency of Pb(II) ions using the Fe_3O_4-CaAlg sorbent were studied using 50 mg of Fe_3O_4–CaAlg sorbent, 30 min extraction time, 10 mL of 0.1 M nitric acid as desorption solvent and 10 min of desorption time (sonication assisted). It was found that the Fe_3O_4-CaAlg MSPE of Pb(II) ions was highly dependent on sample solution pH. Optimum Pb(II) extraction efficiency occurred at pH 6 using 150 mL sample volume and the Fe_3O_4–CaAlg MSPE method was found to be affected by the co-existence of Na^+, K^+, Mg^{2+} and Cl^- ions in solution. The linearity of the Fe_3O_4-CaAlg MSPE method was in range of 60 – 500 µg/L with coefficient of determination of 0.9790. The limit of detection and limit of quantification were 44.5 µg/L and 76.7 µg/L, respectively. Repeatability (n = 3) of the Fe_3O_4–CaAlg MSPE method as measured by relative standard deviation was 4.36%. The Fe_3O–CaAlg MSPE method was applied to two real water samples namely UTM lake and laboratory tap water using optimum conditions. Lake water recovery for Pb(II) ions (spiked level 400 µg/L) was 110.38% (RSD 3.04%, n = 3) while the recovery for Pb(II) ion from tap water (spiked level 400 µg/L) was 104.2% (RSD 3.53%, n = 3). Excellent recovery and precision indicates that the proposed Fe_3O_4–CaAlg MSPE method is a good alternative sorbent for Pb(II) ion analysis from water samples.

Keywords: Pb(II) ions, magnetic solid phase extraction, flame atomic absorption spectroscopy, magnetite calcium alginate, water samples

1. INTRODUCTION

Heavy metal contamination such as lead (II) ions in water is very dangerous to human body and environmental health. The trace concentration of heavy metals such as lead(II) ion is toxic. Their accumulation can cause poisoning, cancer and brain damage (Mashhadizadeh et al., 2013). This Pb(II) ions might come from piping in the process of transferring of water from treatment centre process and might lead to our consumption. Mostly the long transferring pipe is made up of lead and it might contaminate the water along the way of transportation of water. The accumulation from natural water resources such as river and estuaries also is a concern. The level of heavy metal in water must be lower than drinking water standard according to Interim National Water Quality Standard (INWQS). Allowable level of Pb(II) ions in drinking water is as low as 0.05 ppm (Kumar and Puri, 2012). Thus, the extraction and removal of heavy metals from water is important and getting more worldwide attention (Mashhadizadeh et al., 2013).

Usually, working in trace analysis field, preconcentration and separation of the trace element from the matrices is very important to improve the limit of detection and the selectivity of determination on the trace elements (Zhai et al., 2012). Common pretreatment methods that are usually used are Soxhlet extraction, steam distillation, hydro-distillation and solvent extraction. These methods are known as conventional methods and it is labour-intensive, time consuming and large amount of solvent and samples are required (Nie et al., 2015). In the midst to overcome the disadvantages and develop greener separation techniques, MSPE was developed, which is known to be more cost effective, simpler, less time and energy consuming compared to SPE. MSPE is generally based on the magnetic particle that is applied as adsorbent. The magnetic sorbent material effectively works due to their unique magnetic properties and it has low cytotoxicity. However, the agglomeration and rapid degradation of pristine magnetic nanoparticles (MNPs) was the major obstacle that needs to be overcome.

The MNPs modified by coating with a biopolymer has a great future in material field research. Thus, modification is made on the naked magnetite Fe3O4 NPs by encapsulating it with various coating ligands such as calcium alginate (CaAlg) (Asgharinezhad et al., 2014). This modification is done due to metal oxide NPs provide large surface area which may cause the unprotected magnetic NPs exposed to oxygen in the air and can be easily aggregated. This modification also can increase the efficiency of adsorbent, thus increase the extraction efficiency and eliminate this limitation as it can dispersed completely in water and adsorb the analyte quickly from the matrices (Jeddi et al., 2014). The combination of Fe_3O_4 –CaAlg with MSPE method would give higher extraction efficiency (Yamini and Faraji, 2014).

2. EXPERIMENTAL

2.1. Chemicals and Reagents

The chemicals and reagents involved in this experiment were commercial and analytical reagent grade and used directly without any further purification. Deionized water was used for optimization process while the collected real samples were used in the application part. The Pb(II) solution (1000 mgL-1) was purchased from Certipur® AAS Standards and used as stock solutions. The lead(II) nitrate, $Pb(NO_3)_2$ was purchased from Sigma-Aldrich (Milwaukee, USA). 65% of Nitric acid and NaOH pellet were purchased from QRec (Asia) Sdn. Bhd. (Selangor, Malaysia). In the synthesis of magnetite-calcium alginate adsorbent, the sodium alginate powder was purchased from QRec (Asia) Sdn Bhd. (Selangor, Malaysia), commercial Fe_3O_4 from Bendosen (Selangor, Malaysia) and calcium chloride, $CaCl_2.2H_2O$ was come from HmbG® Chemicals (Selangor, Malaysia). Fe_3O_4-CaAlg was synthesized in laboratory of Faculty of Science. The lake and tap water samples were collected from the main lake and laboratory in Universiti Teknologi Malaysia (Johor, Malaysia) respectively.

2.2. Instrumentation

The instrument used for detection of Pb(II) ions is a PinAAcle 900T atomic absorption spectrometer equipped with a deuterium background correction. This AAS is equipped with lead hollow-cathode lamp as the radiation source to measure absorbance at 283.31 nm under air/acetylene flame. While, for characterization of the synthesized adsorbent, Fe_3O_4-CaAlg, a JEOL JSM-6390LV Scanning Electron Microscope (SEM) and a Perkin-Elmer TM 400 Fourier Transform Infrared (FTIR) (Waltham, MA, USA) were used. Different magnifications of SEM were used within range ×5- 15k magnification while for FTIR analysis, a KBr plate was used. The pH 700 meter used for adjustment of pH is from Eutech instrument.

2.3. Preparation Series of Standard and Real Water Samples

The 1000 ppm stock solution for Pb was provided from Certipur® AAS Standards. The standard solution was prepared from the stock solution (1000 ppm) by serial dilution. From 1000 ppm stock solution, it was intermediate diluted to 100 ppm solution. Then, from 100 ppm, it was diluted to 50 ppm and then to10 ppm. The standard solution was used in calibration of the instrument and method. It was prepared in different concentrations which are 1 ppm, 2 ppm, 3 ppm, 4 ppm, and 5 ppm from 10 ppm stock solution earlier. River water sample was collected from Sungai Skudai (Johor, Malaysia). The lake water sample was from the main lake of Universiti Teknologi Malaysia, Skudai while fresh tap water was obtained from the laboratory of Department of Chemistry, Universiti Teknologi Malaysia, Skudai. The samples collected was preserved in acidic condition with pH 2 using a solution of 0.1 M HNO_3 to maintain the initial concentration and stored in freezer at -20ºC until analysis day.

2.4. Synthesis of Fe_3O_4-Calcium Alginate

An amount of 4.5 g of the prepared NaAlg was accurately weighed and dissolved in 200 mL of deionized water with continuous stirring using magnetic stirrer. At the same time, $CaCl_2$ solution was prepared by mixing 3.3 g of $CaCl_2$ powder in 150 mL deionized water and left to stir. Then, for encapsulation process to form Fe_3O_4-CaAlg adsorbent, 0.5 g of commercial Fe_3O_4 powder was first dissolve in deionized water and easy to be mixed with alginate later on. The Fe_3O_4 solution was prepared by diluting first the commercial Fe_3O_4 powder with deionized water to form solution. It was added slowly into NaAlg and form Fe_3O_4-NaAlg. The Fe_3O_4-NaAlg mixture then was slowly dropped into $CaCl_2$ solution and the beads will form immediately shows formation of Fe_3O_4-Ca Alg beads. Lastly, the beads were thoroughly rinsed with deionized water to eliminate residues of calcium and chloride ions. Then, the Fe_3O_4-Ca Alg beads were dried in the oven for 24 h to remove the water residue.

2.5. MSPE of Fe_3O_4-Ca Alg

The procedure in MSPE techniques was started by adding appropriate amount of adsorbent materials (50 mg) into 150 mL of water samples and was shakened for 30 min at 250 rpm. It was left to stand for some time and the adsorbent was collected using an external magnet. Then, 10 mL of 0.1M HNO_3 as desorption solvent was added into adsorbent and was sonicated for 10 min (Tubah 2015). After 10 minutes sonication, the external magnet was used again to separate the adsorbent material and desorption solvent. The 10 mL desorption solvent was collected and the solvent was analyzed by FAAS.

2.5. Optimization of Extraction Conditions

In this study, parameters optimized were effect of sample volume, sample solution pH and coexistence ions on the Fe3O4-CaAlg adsorbent. Other parameters of MSPE were kept constant: 30 min extraction time, 50 mg adsorbent mass, 10 mL desorption solvent using 0.1 M HNO3 solution, 10 min sonication assisted desorption of sorbed analyte (Tubah, 2015).

3. RESULTS AND DISCUSSION

3.1 FTIR Characterization of Synthesized Fe3O4-CaAlg

The FTIR spectrum of commercial Fe3O4 is given in Figure 1(a) showed the presence of the stretching mode of Fe-O at 579.20 cm-1. The broad peak from the spectrum at 2330.96 cm-1 might due to presence of moisture from the commercial samples. Figure 1(b) is the FTIR spectrum for calcium alginate which shows the functional groups present in the materials strong OH band at 3439.15 cm-1, medium C-H band at 2926.90 cm-1 and medium C-O bands at 1628.34 cm-1 and 1424.91 cm-1. Figure 1(c) shows the FTIR spectrum for Fe3O4-CaAlg. Generally the spectrum is dominated by alginate peaks (-OH band at 3446.92 cm-1), (C-O bands at 1629.73 cm-1 and 1384.39 cm-1), and (C-H band at 2925.79 cm-1). However, the presence of small peak of Fe-O band at 617.73 cm-1 showed the presence of Fe3O4- MNP. The small peak intensity is probably due to full-coating of the MNP with Ca-Alg.

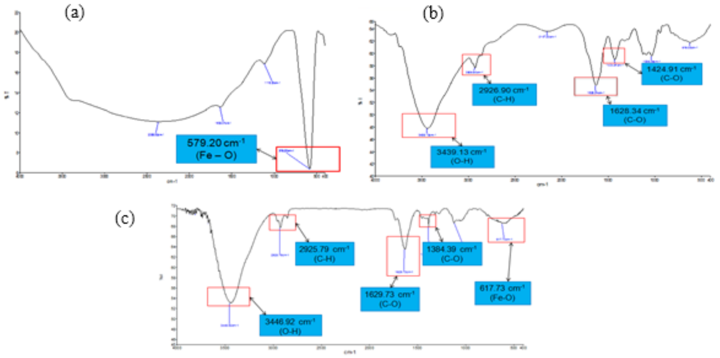


Fig. 1 FTIR Spectrum for (a) Fe3O4 (b) CaAlg (c) Fe3O4-CaAlg

3.2 SEM Characterization

SEM characterization was conducted on the synthesized Ca Alg and Fe3O4-CaAlg. Magnifications used were in range ×5 to ×15k and at acceleration voltage of 10 kV. Figure 2 show the surface morphology of Ca-Alg bead without the MNP. Generally the beads are 10,000 µm in diameter. The surface of the beads is rugged without presence of distinct pores.

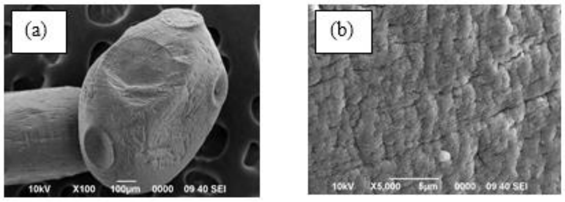


Fig. 2 Surface Morphology of Calcium Alginate (CaAlg) bead at 10 kV with (a) ×100 Magnification and (b) ×5,000 Magnification

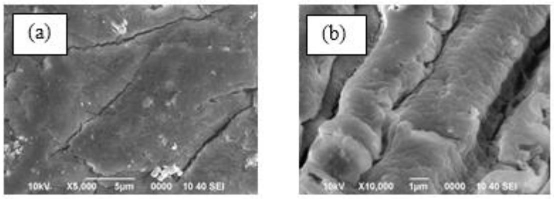


Fig. 3 Surface Morphology of Fe3O4-CaAlg at 10 kV with (a) ×5,000 magnification and (b) ×10,000 Magnification

The surface morphology of Fe3O4-CaAlg (Figure 3) shows that the Fe3O4-CaAlg was also rugged with an uneven structure on the surface of the bead.

3.3 Effect of Sample Volume

Theoretically, high sample volume is needed for higher enrichment. In the study on effect of sample volume on the extraction of Pb(II) ions, different volumes of sample were optimized which were 50 mL, 100 mL, 150 mL, 200 mL and 250 mL with 0.5 mg/L solution of Pb(II) ions. The aim of this optimization parameter is to study the effect of sample volume on the extraction efficiency of the adsorbent. A 50 mg of Fe3O4CaAlg adsorbent was added into a series of different volume of samples. The best result for adsorption of Pb(II) ions was achieved using 150 mL of sample volume (Figure 4). An increased in absorbance reading was observed when sample volume was increased from 50 mL to 150 mL but started to gradually decrease from 200 mL to 250 mL. The increased in absorbance might be due to the amount of adsorbent was sufficient to adsorb the amount of Pb(II) ions in solution until it reach the limit of adsorption at 150 mL. At 200 mL sample volume, breakthrough volume of the adsorbent most probably has been reached, thus the decrease in absorbance reading. Thus, 150 mL sample volume was used as the optimum for extraction of Pb(II) ions using the Fe3O4-CaAlg adsorbent.

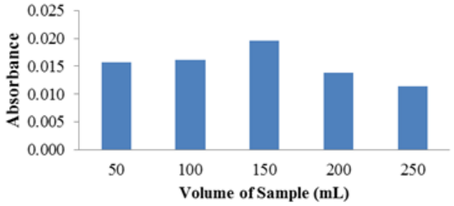


Fig. 4 Effect of Sample Volume on MSPE Efficiency (measured by absorbance) of Fe3O4-CaAlg MSPE for Pb(II) Ions from Deionized Water Samples. MSPE conditions: initial concentration = 0.5 mg/L, extraction time = 10 min, mass of adsorbent = 50 mg. MSPE Desorption conditions: Concentration of desorption solvent = 0.1M HNO3, volume of desorption solvent = 10 mL, desorption time (sonication assisted) = 10 min.

3.4 Effect of Sample Solution pH

Sample solution pH is one of the important parameters in the extraction of Pb(II) ions due to the changes in charge density of the MNPs adsorbent (Yamini and Faraji, 2014). The acidity of water solution plays an important role in extraction process. In this study, the chosen sample solution pHs to be optimized were 2, 4, 6 and 8 with a 0.5 mg/L Pb(II) ions solution (Figure 5). In this optimization process, pH higher than 8 was not optimize because in basic conditions precipitation of metal hydroxide, $Pb(OH)_2$ occurred in the solution (Abd Ali *et al*., 2016).

Figure 5 showed that the increased of absorbance was observed with increasing pH of sample solution. At pH 2, the absorbance was lowest absorbance. The lower absorbance might be due to strong competition between Pb(II) ions and hydrogen ions which compete for the same adsorption sites (Abd Ali *et al*., 2016). In this condition, most of the functional groups of the components are protonated and only a few of ionizable groups were left which means that the adsorbent do not have sufficient capacity for adsorption at acidic condition for preconcentration of Pb(II) ions (Mashhadizadeh *et al*., 2014). At pH 8, the metal ions started to precipitate into metal hydroxide. So, the most efficient pH for extraction of Pb(II) ions are pH 6 which showed a good absorbance for most metal ions extractions (Mashhadizadeh *et al*., 2014).

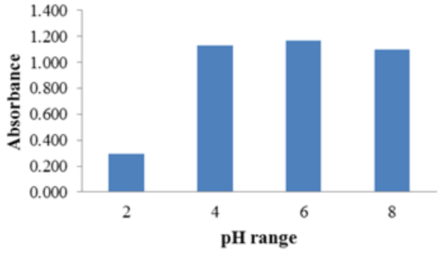


Fig. 5 Effect of sample solution pH on Fe_3O_4-CaAlg MSPE for Pb(II) ions from deionized water samples. MSPE conditions: initial concentration = 0.5 mg/L, extraction time = 10 min, mass of adsorbent = 50 mg, Sample volume = 150 mL. MSPE desorption conditions: Concentration of desorption solvent = 0.1M HNO_3, volume of desorption solvent = 10 mL, desorption time (sonication assisted) = 10 min.

3.5 Effect of Co-existence Ions

Three types of salt (NaCl, KCl and $MgCl_2.2H_2O$, initial concentrations used for each salt before diluting is 100 ppm) were mixed with the sample solution to study whether the addition of ions such as Na^+, K^+, Mg^{2+} and Cl^- affect the extraction efficiency of the Fe_3O_4-CaAlg MSPE for Pb(II) ions from water matrices (Figure 6). In this study, the MSPE procedure was performed using the optimum conditions thus far obtained. Optimization process was performed using a 0.5 mg/L solution of spiked Pb(II) ions. The results obtained indicate that these co-existence ions seems to influence the extraction efficiency of the Fe_3O_4-CaAlg sorbent for Pb(II) ions. Maximum absorbance of Pb(II) ions was observed with 10 ppm total salt concentration.

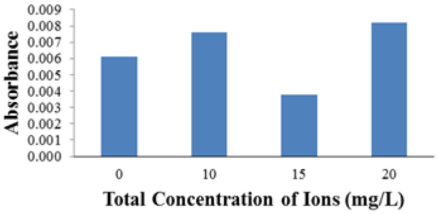


Fig. 6 Effect of co-existence ions (Na^+, K^+, Mg^{2+} and Cl^-) on extraction performance of Fe_3O_4-CaAlg MSPE for Pb(II) ions from deionized water samples. MSPE conditions: extraction time = 10 min, mass of adsorbent = 50 mg, sample volume = 150 mL and sample solution pH 6. MSPE desorption conditions: Concentration of desorption solvent = 0.1M HNO_3, volume of desorption solvent = 10 mL, desorption time (sonication assisted) = 10 min.

3.6 Method Validation

From the result of optimization parameters on Fe_3O_4-CaAlg MSPE, the optimum MSPE conditions are 150 mL sample volume and sample solution pH 6 using 30 ppm salt solutions. The MSPE method was validated for linearity, limit of detection (LOD), limit of quantification (LOQ) and precision (repeatability). Linearity range was from 60 to 500 µg/L and coefficient of determination, R^2 was 0.9790. The calculated Fe_3O_4-CaAlg MSPE method LOD and LOQ were 44.5 µg/L and 76.7 µg/L, respectively. Good repeatability (RSD of 4.36%, $n = 3$) was obtained.

3.7 Application of Fe_3O_4-Calcium Alginate MSPE on Analysis of Pb(II) Ions from Lake and Tap Water Samples

The UTM lake and laboratory tap water samples were analyzed for Pb(II) ions using the developed Fe_3O_4-Calcium Alginate MSPE method under optimized condition. No detectable Pb(II) ions was observed in both samples analysed. In the recovery study, the sample solution was spiked to give a final concentration of 400 µg/L. The result obtained is summarized in Table 1. Excellent recovery and precision indicates that the proposed Fe_3O_4–CaAlg is a good alternative candidate for Pb(II) ion analysis from water samples.

Table 1 Percentage Recoveries of Pb(II) ions from Water Samples Spiked at 400 µg/L using Fe_3O_4-CaAlg

Water Sample	Recoveries (%)	% RSD (*n*=3)
Lake	110.38	3.04
Tap	104.23	3.53

4. CONCLUSION

Fe_3O_4-CaAlg was successfully prepared and used as an MSPE adsorbent for Pb(II) ions analysis from water samples. It was successfully characterized using FTIR and SEM. Three parameters that highly affected the developed MSPE method were successfully obtained to achieve high efficiency of MSPE extraction efficiency (based on absorbance) for Pb(II) ions . Optimum conditions were achieved with 150 mL of sample volume at sample solution pH 6 at 30 min extraction time, 50 mg adsorbent, 10 mL of 0.1 M HNO_3 as desorption solvent and 10 min sonication assisted desorption time) . The co-existence of several ions (Na^+, K^+, Mg^{2+}, Cl^{-1}) in sample solution was found to affect the performance of the MSPE adsorbent. 20 ppm salt concentration was found to give the highest absorbance for Pb(II) ions from water. The developed Fe_3O_4-CaAlg MSPE method was successfully applied to the determination of Pb(II) ions in laboratory tap and UTM lake water samples due to its sensitivity, selectivity, robustness, simplicity and reliability to the matrices.

From the result obtained, linearity of the developed MSPE method was in the range 60 to 500µg/L with a coefficient of determination of 0.9790. The limit of detection (LOD) and limit of quantification (LOQ) obtained for the developed MSPE method were 44.5 µg/L and 76.7 µg/L, respectively. The LOD and LOQ obtained is applicable to real sample analysis as it is below the allowed maximum residue limit. The result shows good repeatability (RSD 2.54%, $n = 3$) of the developed MSPE method. The application of Fe_3O_4-CaAlg MSPE method to two real water samples (UTM lake and laboratory tap water) was successfully performed using the optimum MSPE conditions. Good recoveries and precision were obtained for UTM lake water (110.38%, RSD 3.04%) and tap water samples (104.23%, RSD 3.53%) at a spiking level of 400 µg/L of Pb(II) ions.

The developed MSPE method using Fe_3O_4–CaAlg has high potential as an alternative adsorbent for Pb(II) ions analysis from water samples. The Fe_3O_4-CaAlg MSPE method is simple, rapid, green, and inexpensive method. The new adsorbent is highly recommended to be used in MSPE for preconcentration of heavy metals ions from aqueous samples.

REFERENCES

[1] Abd Ali, L. I., Wan Ibrahim, W. A., Sulaiman, A., Kamboh, M. A., Sanagi, M. M. (2016). New chrysin-functionalized silica-core shell magnetic nanoparticles for the magnetic solid phase extraction of copper ions from water samples. *Talanta, 48*, 191-199.

[2] Asgharinezhad, A. A., Ebrahimzadeh, H., Rezvani, M., Shekari, N., Loni, M. (2014). A Novel 4-(2-Pyridylazo) Resorcinol functionalized magnetic nanosorbent for selective extraction of copper ion and lead ions from food and water samples. *Food Additives And Contaminant Part A*, *31(7)*, 1196-1204.

[3] Izy Zaiha Tubah (2015). *Ferrite Calcium Alginate as Adsorbent in Magnetic Solid Phase Extraction of Lead(II) Ion in Water Prior to Flame Atomic Absorption Spectroscopy*. Universiti Teknologi Malaysia: Degree Report.

[4] Jeddi, M. Z., Ahmadkhaniha, R., Yunesian, M., & Rastkari, N. (2014). Magnetic solid phase extraction based on modified magnetic nanoparticles for the determination of phthalate diesters in water samples. *Journal of Chromatographic Science*, 1-7, 2014.

[5] Kumar, M., & Puri, A. (2012). A review of permissible limits of drinking water. *Indian Journal of Occupational Environmental Medicine*, 16(1), 40-44.

[6] Mashhadizadeh, M. H., Amoli-Diva, M., Shapouri, M. R., Afruzi, H. (2013). Solid phase extraction of trace amount of silver, cadmium, copper, mercury, and lead in various food samples based on ethylene glycol bis-mercaptoacetate modified 3-(trimethoxysilyl)-1-propanethiol coated Fe_3O_4 nanoparticles. *Journal Of Food Chemistry*, *151*, 300-305.

[7] Nie, J., Teng, Y. J., Li, Z. G., Liu, W. H., & Lee, M. R. (2015). Magnetic nanoparticles used in headspace extraction coupled with DSI-GC-IT/MS for analysis of VOCs in dry traditional chinese medicine. *Chinese Chemical Letters.*

[8] Yamini, Y., & Faraji, M. (2014). Extraction and determination of trace amounts of chloropromazine in biological fluids using magnetic solid phase extraction followed by HPLC. *Journal of Pharmaceutical Analysis*, *4(4)*, 279-285.

[9] Zhai, Y., Han, Q., Duan, S., & He, Q. (2012). Solid phase extraction of trace metal ions with magnetic nanoparticles modified with 2, 6-diaminopyridine. *Microchima Acta*, *178*:405-412.