RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Magnetic Solid Phase Extraction of lead(II) and cadmium(II) on magnetic phosphorus-containing polymer (M-PhCP) to their microsampling flame atomic absorption spectrometric determinations

E. Yilmaz [1], R.M. Alosmanov [2], M. Soylak [1*]

[1] *Erciyes University, Fen Faculty, Department of Chemistry, 38039 Kayseri, Turkey*

[2] *Baku State University, Chemistry Department, Z. Khalilov str., 23, Baku, AZ1148 Azerbaijan*

Abstract

A magnetic solid-phase extraction (M-SPE) procedure on magnetic phosphorus-containing polymer (M-PhCP) was established for separation/preconcentration of trace amounts of lead and cadmium in water samples prior to their microsampling flame atomic absorption spectrometric determination. The separation of lead(II) and cadmium(II) adsorbed as 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol (5-Br-PADAP) chelates on M-PhCP as from the aqueous solution was simply achieved by applying external magnetic field via a piece of permanent magnet. The important analytical factors governing the extraction efficiency such as pH, amount of adsorbent, eluent concentration and volume, vortex time, ligand volume, sample volume, have been investigated and optimized. The influences of matrix components were also searched. The limit of detection (LOD) of Pb and Cd were 2.7 and 1.1 µg L^{-1}, respectively. The accuracy of the proposed method was proved by analysis of TMDA-TMDA-64.2 Lake Ontario water and SPS-WW2 Waste water certified reference materials and addition-recovery tests. The method was successfully applied for the determination of lead and cadmium in water samples.

Keywords: Magnetic phosphorus-containing polymeric sorbent, magnetic solid phase extraction, lead, cadmium, flame atomic absorption spectrometry.

*Corresponding Author, e-mail soylak@erciyes.edu.tr, Tel. /fax: +90 352 4374933.

Introduction

The environmental exposure to the heavy metals is a well known risk factor for human health and they are too harmful to plants and animals.[1,2,3,4,5] Heavy metals like lead and cadmium are extremely toxic even at very low levels for humans and animals, while copper, nickel and zinc plays an important role in several biochemical processes, and their compounds have bactericidal activity.[6,7,8,9] However, if they are in excess, these metals can cause various chronic disorders in human beings.[10] Environmental samples are considered as a main source for human exposure to lead and cadmium. Therefore, monitoring of lead and cadmium in environmental samples is very important to ensure the quality of human health.[11,12,13]

Due to the very low concentrations of heavy metals in real samples, their determinations demand very sensitive analytical techniques including inductively coupled plasma mass spectrometry (ICP-MS), electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and X ray fluorescence (XRF).[14,15,16] However, when compared to flame atomic absorption spectrometry (FAAS), the available analytical techniques have some disadvantages such as its high cost, slowness and greater proneness to matrix interferences as well as their high sensitive advantages.[16,17] FAAS is, in principle, a suitable technique due to the low cost and easy operation. However, FAAS do not have sufficient sensitivity and selectivity for the determination of heavy metals in real samples because of their low concentration, which may be lower than the detection limit of FAAS and matrix effects.[18,19]

A separation/preconcentration procedure is generally required for solve sensitivity and selectivity problems. Several techniques have been developed for separation and preconcentration of trace metals including: cloud point extraction,[20] liquid–liquid extraction,[21] precipitation/co-precipitation,[13] and solid-phase extraction (SPE).[17] SPE are considered superior to other techniques for their simplicity, consumption of small volumes of organic solvent, and ability to obtain a higher preconcentration factor and higher speed.[17,22,23]

Magnetic adsorbents have attracted much attention because of their unique magnetic properties for SPE procedures.[24,25,26,27] In magnetic SPE, magnetic sorbent is added to the sample solution including the target analyte. The analytes are adsorbed onto the magnetic adsorbent whether under mixing or standing. The adsorbent with captured analytes is then isolated from the sample solution by using an appropriate magnet. Finally, the target analytes adsorbed on the adsorbents were desorbed with suitable elution and analyzed an appropriate method.[28,29] The application of magnetic SPE simplifies preconcentration-separation steps for analytes.[28,29] The magnetic adsorbents need not be packed into the cartridge or column, as in traditional SPE, and the phase separation can be realized easily by applying an external magnetic field.

In the present paper, a magnetic phosphorus-containing polymeric sorbent (M-PhCP) was used for magnetic solid phase extraction (M-SPE) of lead(II) and cadmium(II) as 2-(5-bromo-2-pyridylazo)-5-diethylamino-Phenol (5-Br-PADAP) chelates from natural water samples prior to their microsampling flame atomic absorption spectrometric determination of them.

2. Experimental

2.1. Chemicals and solutions

The water used in the experiments was ultrapure water which was prepared using a milli-Q system (18.2 MΩ cm) from Millipore (Bedford, MA, USA).All chemicals used were analytical reagent grade and were used without further purification. Analytical-grade acids and other chemicals used in this study were purchased from Merck, Darmstadt, Germany. The chelating agent, which 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol (5-Br-PADAP) from Sigma-Aldrich (St. Louis, MO, USA), was daily prepared in ethanol as 0.1% (m/v). Working metal ion solutions used for the experiments were prepared by dilution of 1000 mg L^{-1} of stock solutions.

Buffer solutions were prepared by using combination of salts and solutions as follows: phosphate buffer solution (pH 2.0-4.0, sodium dihydrogen phosphate/phosphoric acid), phosphate buffer solution (pH 5.0-7.0 sodium dihydrogen phosphate/disodium hydrogen phosphate). TMDA-64.2 TMDA- 64.2 Lake Ontario water (National Water Research Institute, Ontario, Canada) and SPS-WW2 Waste water (Spectrapure Standards AS, Oslo, Norway) certified reference materials were used.

2.2. Apparatus

A Perkin-Elmer Model 3110 (Norwalk, CT, USA) flame atomic absorption spectrometer equipped with a hollow cathode lamp and an air/acetylene flame as an atomizer was used for the measurements. The continuous aspiration mode was used to measure the metal ions concentration in eluate. A hundred µL of the eluate phase was injected into the FAAS nebulizer by using a home-made micro sample introduction system consist of Teflon funnel and Eppendorf pipette and the peak height was measured.[11,30]

The FT-IR spectra of the phosphorus-containing polymeric sorbent (PhCPS) and magnetic phosphorus-containing polymeric sorbent (M-PhCP) were recorded on a Perkin-Elmer Spectrum 400 ATR-FT-IR spectrometer (Waltham, MA, USA). Scanning electron microscope (SEM) images were obtained on a LEO 440 SEM with an accelerating voltage of 20 kV. For SEM measurements, the samples were covered Au/Pd. The surface area, pore volume and pore width of magnetic phosphorus-containing polymeric sorbent (M-PhCP) was determined by the BET-N_2 method using a Micromeritics Gemini VII analyzer. A pH meter, Sartorious PT-10 (Germany) was used for measuring pH values. VWR international model (Germany) vortex mixer was used during the experimental period.

2.3. Synthesis of magnetic adsorbent

Phosphorus-containing polymeric sorbent was used for magnetic adsorbent as matrix (PhCPS). PhCPS were obtained as described in. [31] 5% solution of polybutadiene in CCl_4 was subjected to oxidative chlorophosphorylation by PCl_3 under the action of oxygen. This resulted in the formation of a modified substance of three-dimensional structure containing functional groups with P–Cl bonds, which were further processed with water for hydrolysis. The adsorbent was purified and dried at 50 °C in a vacuum cabinet.[31] Its structure was studied by NMR in solid phase.[32] It has been established that the PhCPS has a three-dimensional structure (crosslinked polymers) and contain the phosphonate and phosphate groups. Magnetic adsorbent has been prepared as follows: at first ferric and ferrous chlorides (molar ratio 2:1) were dissolved in water at a concentration of 0.3 M iron ions. Then, this mixture was added on to PhCPS. The volume of solution was 100 mL and amount of PhCPS was 1.0 g. The suspension was stirred during two hours. Then PhPCS was separated from the aqueous solution and dried in air. Then 50 ml of sodium hydroxide with a concentration of 4 M was added to air-drying adsorbents. Argon gas was passed in mixture and the reaction was allowed to proceed for 1 hour at 80 °C under constant and vigorous stirring in reflux equipment. The obtained pure black magnetic phosphorus-containing polymeric sorbent (M-PhCP) separated using a magnet and washed several times with water and ethanol, and then finally dried in a vacuum oven at 50 °C.

2.4. General procedure

25 mL of model solutions containing 20 µg lead(II) and 10 µg cadmium(II) ions, 100 µl of 0.1 % 5-Br-PADAP and 5 mL phosphate buffer were transferred to 50 ml conical-bottom glass centrifuge tube and pH of the solutions were adjusted to pH 6.0. Then, 100 mg of magnetic adsorbent were added, and the solution was mixed by using a vortex agitator for 3 min to facilitate adsorption of the metal ions onto the adsorbent. A neodymium magnet was subsequently held around the test tube for easily and quickly collection of the magnetic adsorbent at the bottom of the test tube. Then, the supernatants were decanted directly. A 5.0 mL 0.5 mol L^{-1} HNO_3 in acetone solution was added as eluate and mixed again for 1 min. The magnetic adsorbent was collected from eluate with the magnet. Then, the eluate was taken the other tube by using pipette. Acetone in the eluate was evaporated till approximately 500 µL. The final volume was completed to 500 µL with acetone in a HPLC vial which has 500 µL. Finally, 100 µL of the eluate was taken using a micropipette and injected into the microinjection system coupled with FAAS nebulizer. The peak height in continuous aspiration mode was measured.

2.5. Analysis of real samples

River water and dam water from Kayseri, waste water sample from plants located in Kayseri Organized Industrial Area and well water from Ankara, Turkey were collected. Samples used were collected in pre-washed polyethylene containers and were filtered through a Millipore cellulose membrane filter (0.45 mm of pore size). Then, the developed magnetic SPE method was applied to the water samples.

The developed magnetic SPE method was also applied to TMDA 64.2 Lake Ontario water and SPS-WW2 Waste water certified reference materials. The analytes in eluate were determined with flame AAS by using microsampling system.

3. Results and discussion

3.1. Characterization of Magnetic Adsorbent

The FT-IR spectra of phosphorus-containing polymeric sorbent (PhCPS) and magnetic phosphorus-containing polymeric sorbent (M-PhCP) (A and B) are shown in Fig. 1. In the IR spectrum of PhCPS (A), the typic bands can be assigned as follows: O-H: 3343 cm^{-1}, C-H: 2978 cm^{-1}, 2935 cm^{-1}, O-H (P-O-H): 2862 cm^{-1}, 2494 cm^{-1} P=O (Resonance state): 1622 cm^{-1}, P=O: 1183 cm^{-1}, C-O (P-C-O): 1050 cm^{-1} and C-Cl: 495 cm^{-1}, respectively. In the IR spectrum of M-PhCP (B), the sorption peak of OH of PhCPS had been remarkably weakened after the process of making magnetic because of change hydrogen with iron groups. Fe-O has the characteristic band at 546 cm^{-1} [33] and also this indicates that Fe_3O_4 molecules are successfully formed within the structure of the phosphorus-containing polymeric sorbent.

Scanning electron microscopy (SEM) micrographs presented in Fig. 2 shows the porous surfaces structure of the PhCPS (A) and M-PhCP (A). The morphology of the PhCPS and M-PhCP shows some differences. The PhCPS surface is quite rough, providing a large exposed surface area for adsorption of metal-ligand complex. To investigate, the presence and distribution of magnetic particles in the magnetic phosphorus-containing polymer, elemental mapping image (EMI) method was carried out by using SEM-EDX analysis. For this purpose, the elemental mapping image of the iron element was performed (Figure 3). The obtained elemental mapping image indicates that the iron magnetic particles are homogeneously dispersed on the phosphorus-containing polymer. The magnetic phosphorus-containing polymer was also analyzed for elemental composition by SEM-EDX. The sample were covered Au. The obtained spectrum was given in Fig. 4. The amount of iron was found as 6.8 Wt, %.

The structure of the phosphorus-containing polymer (A) and magnetic phosphorus-containing polymer (B) was characterized by XRD and the diffractogram is given in Fig. 5. There are four types of iron oxides commonly formed including magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3) and goethite (FeO(OH)). Among them, only magnetite and maghemite are magnetic. The XRD pattern of the magnetic phosphorus-containing polymer displays four main diffraction peaks at $2\Theta= 31.8^o$, 34.3^o, 45.5^o, 55.3^o and 62.4^o that can be assigned to maghemite or magnetite. Other peaks are also observed at 2Θ = 19.1^o, 33.3^o, 42.2^o and 59.5^o for the magnetic phosphorus-containing polymer, which may be related to the presence of geotite. The diffraction pattern of magnetic phosphorus-containing polymer is close to the standard pattern for JCPD. It is clearly seen that the particles do not show sharp diffraction peaks. Instead, a broadband appears. This is typical for amorphous materials and also for ultrafine crystalline materials where diffraction peaks cannot be well resolved.

From IR spectrum that the typical bands for phosphorus-containing polymer (O-H, C-H, O-H (P-O-H): P=O (Resonance state) P=O: 1183 cm^{-1}, C-O (P-C-O) and C-Cl: 495 cm^{-1}) were also appeared for magnetic phosphorus-containing polymer. The IR spectrum for magnetic phosphorus-containing polymer shows that the polymeric parts of the magnetic phosphorus-containing polymer are effective for the adsorption of analytes as their 5-Br-PADAP chelates. The van der waals interactions are important for adsorption studies. The functional groups of phosphorus-containing polymer provide effective van der waals interactions between analytes-5-Br-PADAP chelates and adsorbent.

The adsorption efficiency is related to its internal surface area and pore volume. The BET surface area, pore volume and pore width of the M-PhCP was found to be 7.53 $m^2\ g^{-1}$, 0.00535 $cm^3\ g^{-1}$ and 2.84 nm, respectively. The BET isotherm of M-PhCP sample in Fig. 6 shows that the contribution of mesopores to the total surface area and pore volume is significantly higher than that of macropores.[34]

3.2. Optimization of extraction parameters

The pH of sample solution has an important role in extraction studies of metal ions at trace levels.[34,35,36,37,38,39] The pH of model solutions containing 20 μg lead(II) and 10 μg cadmium(II) was studied within the range of 2.0-8.0 using buffer solutions and then the separation/preconcentration procedure described was applied. As can be seen in Fig. 7, the quantitative recoveries for analyte ions were obtained in the pH 6.0. Hence, pH 6.0 was used in all experiments as optimum value.

Compared to conventional adsorbents, magnetic adsorbents have some advantages including high extraction capacity, rapid extraction dynamics and high extraction efficiencies.[29, 40, 41, 42, 43, 44] The amount of the magnetic adsorbent was studied in the range of 25–100 mg of magnetic adsorbent. The recoveries for Pb(II) and Cd(II) were increased and to reach quantitative value at 100 mg of magnetic adsorbent. Therefore, 100 mg of adsorbent was selected further experiments.

The recoveries of analytes by the iron species only were 75% and the recoveries of analytes on phosphorus-containing polymer with ligand without magnetic properties was lower than 50 %. The recoveries of analytes on magnetic phosphorus-containing polymer with ligand (presented system) were quantitative (>95%).

The influences of various eluents on the recoveries of Pb(II) and Cd(II) ions from magnetic phosphorus-containing polymeric sorbent were also examined. The results are summarized in Table 1. It should be pointed out that it can be possible regeneration of the magnetic property of adsorbent due to dissolution of Fe_3O_4 in high acid concentration. Hence, the low concentrations of HNO_3 were examined in this study. The recoveries of analyte ions were quantitative with 0.5 M HNO_3 in acetone. The recoveries were not quantitative for the other eluents. 0.5 M HNO_3 in acetone was used as eluent all further works for quantitative recovery of metal ions from M-PhCP. At the same time, the effect of the eluent volume on the recoveries of Cd(II) and Pb(II) was studied. It was found that quantitative recoveries could be obtained with 5.0 mL of 0.5 M HNO_3 in acetone solution and more than 5.0 mL. Therefore, 5.0 mL of eluent was used in the following experiments.

In order to obtain hydrophobic metal complex, 5-Br-PADAP was used as complexing agent. The effects of the amounts of 5-Br-PADAP on the recoveries of the analytes were also examined with model solutions containing 20 μg lead(II) and 10 μg cadmium(II) in the range of 0.0–0.5 mg of 5-Br-PADAP. The results are shown in Fig. 8. The results are not quantitative without ligand. The quantitative recoveries were obtained by using 0.1 mg of 5-Br-PADAP. Hence, 0.1 mg of 5-Br-PADAP was used for further study.

In order to obtain high preconcentration factor, [45, 46, 47, 48, 49, 50, 51, 52] the magnetic SPE method was applied 10, 15, 20, 30 and 40 mL of sample solution. The quantitative recoveries for analytes could be obtained by using 100 mg of M-PhCP when sample volume was 40 mL. Preconcentration factor was 80. Therefore, the developed method is very suitable for preconcentration of trace lead and cadmium from large volumes of sample solution.

The effect of common interfering ions on the recoveries of the Pb(II) and Cd(II) ions was also examined. The obtained results are given in Table 2. The recoveries of all analyte ions were quantitative for the given concentration of interfering ions. The results demonstrate that thousand folds excess of the analyte ions have no effect on the preconcentration and determination of the Pb(II) and Cd(II).

3.3. Analytical performance

The analytical features of the suggested method were evaluated under the optimum conditions. The cycle results show that the M-PhCP adsorbent is stable up to 100 runs without decrease in the recoveries of Pb(II) and Cd(II). The average ± standard deviation of Pb (II) and Cd(II) recoveries after 100 extraction/elution cycles were found to be 100±0 and 97±1, respectively.

The calibration equations were [$A = 0.0023 + 0.0053C$] for lead and [$A = 0.0002 + 0.2216C$] for cadmium where A is the absorbance and C is iron concentration in mg L^{-1} linear with correlation coefficients of 0.9980 and 0.9978, respectively. The detection limits of the analytes, which defined as 3 times the signal/slope (slope of calibration curve), were 2.7 and 1.1 µg L^{-1} for Pb(II) and Cd(II). The quantification limits, which defined as 10 times the signal/slope (slope of calibration curve), were 9.1 and 3.6 µg L^{-1} for Pb(II) and Cd(II). The relative standard deviations (RSD, %) ,evaluated using the results of the analysis of seven replicates containing 30 µg L^{-1} of Pb(II), and Cd(II), were 3.7 and 4.6, respectively. The preconcentration factor (PF= the ratio of the highest sample volume to the eluent volume) was 80. Consumptive index (CI) is another effective way to evaluate the analytical performance of preconcentration system. CI were also determined by using slope of sample volume (SV) to experimental preconcentration factor (CI= SV/PF). CI was found as 0.5 mL.

3.4. Analytical applications

To evaluate the accuracy of the developed method, the TMDA 64.2 environmental water and SPS-WW2 waste water certified reference materials were analyzed, and the analytical results with the standard deviations are shown in Table 3. It was found that there were no significant difference between the results obtained and the certified results.

To further ensure the accuracy of the magnetic SPE method, the developed method was also applied to the analysis of four water samples corresponding to the CRMs and the analytical results along with the recoveries for the spiked waters are given in Table 4. As it can be seen in Table 4, a good correlation is between the added and recovered amount of lead and cadmium ions. The results for analyzing of certified reference materials and addition-recovery studies show that the developed magnetic SPE method was reliable and independence from effects of the matrix for determination of lead and cadmium in water samples.

4. Conclusion

In this study, a new magnetic phosphorus-containing polymeric sorbent were successfully used as a new sorbent in solid phase extraction for simple, fast and efficient preconcentration of trace Pb and Cd from environmental water samples without matrix interferences. The new solid-phase extractor, which has good physical and chemical properties like durability, porosity and purity and the most important advantage of this magnetic adsorbent, is resistant in mineral acids, bases and organic solvents for a long time for lead and cadmium determination in water samples by FAAS was designed

The most important advantages of the developed method compared with other preconcentration methods in literature are: rapid collection of analyte from adsorbent by using of magnet elution, which eliminates the time-consuming column passing or filtration operation, when compared with the column and filtration operation, a few and adsorbent requirements and low limit of detection for analytes. The analyses of certified reference materials and recovery tests show that the developed method can be used for the rapid preconcentration/separation of Pb(II) and Cd(II) in various water samples.

References

1 M. Yaman and A. Sasmaz, Spectrosc. Spectral. Anal., 2013, **33**, 1.

2 S. Vellaichamy and K. Palanivelu, J. Hazard. Mater., 2011, **185**, 1131.

3 M. Tuzen and M. Soylak, Food Chem., 2007, **101**, 1378.

4 A. Baran, E. Bicak, S.H. Baysal and S. Onal, Bioresour. Technol., 2006, **98**, 661.

5 M. Tuzen, A. Sari, D. Mendil and M. Soylak, J. Hazard. Mater., 2009, **169**, 263.

6 M. Soylak, S. Saracoglu, U. Divrikli, and L. Elci, Trace Elemen. Electroly., 2001, **18,** 47.

7 F. Shah, E. Yilmaz, T. G. Kazi, H. I. Afridi and M. Soylak, Anal. Methods., 2012, **4**, 4091.

8 J. A. Baig, T. G. Kazi, A. Q. Shah, G. A. Kandhro, H. I. Afridi, M. B. Arain, M. K. Jamali, and N. Jalbani. Ecotox. Environ.Safe., 2010, **73**, 914.

9 P. Bulai, C. Balan, C. Cojocaru, and M. Macoveanu, Environ. Eng. Manag. J., 2009, **8**, 1413.

10 S. Tajik and M. A. Taher, Desalination, 2011, **278**, 57.

11 M. Ghaedi, H. Tavallali, A. Shokrollahi, M. Zahedi, M. Montazerozohori and M. Soylak, J. Hazard. Mater., 2009, **166**, 1441.

12 Q. Li, Y. Chen, H. Fu, Z. Cui, L. Shi, L. Wang and Z. Liu, J. Hazard. Mater., 2012, **227–228**, 148.

13 C. Duran, D. Ozdes, D. Sahin, V. N. Bulut, A. Gundogdu and M. Soylak, Microchem. J., 2011, **98**, 317.

14 C. Karadas, Water Air Soil Pollut., 2014, **225**, 2150.

15 D.K. Acar, and D. Kara, Water Air Soil Poll., 2014, **225**, 1864.

16 M. Tuzen, I. Karaman, D. Citak, and M. Soylak, Food Chem. Toxicol., 2009, **47,** 1648.

17 E. Sahmetlioglu, E. Yilmaz, E. Aktas and M. Soylak, Talanta, 2014, **119**, 447.

18 Y.B. Zhu, Bunseki Kagaku, 2007, **56**, 895.

19 M. Rajabi, S. Asemipour, B. Barfi, M. R. Jamali and M. Behzad, J. Mol. Liq., 2014, **194**, 166.

20 I. López-García, Y. Vicente-Martínez and M.Hernández-Córdoba, Spectrochim. Acta B., 2014, **101**, 93.

21 R. Lertlapwasin, N. Bhawawet, A. Imyim and S. Fuangswasdi, Separ. Purif. Technol., 2010, **72**, 70.

22 M. Krawczyk, M. Jeszka-Skowron and H. Matusiewicz, Microchem. J., 2014, **117**, 138.

23 J. Sun, Q. Liang, Q. Han, X. Zhang and M. Ding, Talanta, 2015, **132**, 557.

24 M. Rezvani, A. A. Asgharinezhad, H. Ebrahimzadeh and N. Shekari, Microchim. Acta, 2014, **181**, 1187.

25 H. Parham, N. Rahbar, Talanta, 2009, **80**, 664.

26 L. Chen, T. Wang and J. Tong, TrAC-Trend. Anal. Chem., 2011, **30**, 1095

27 M. H. Mashhadizadeh and Z. Karami, J. Hazard. Mater., 2011, **190**, 1023.

28 Y. Wang, X. Luo, J. Tang, X. Hua, Q. Xua and C. Yang, Anal. Chim. Acta, 2012, **713**, 92.

29 I. S. Ibarra, J. A. Rodriguez, J. M. Miranda, M. Vega and E. Barrado, J. Chromatogr., 2011, **1218A**, 2196.

30 M. Soylak and E. Yilmaz, Desalination, 2011, **275**, 297.

31 Patent of Azerbaijan Republic, No: 0108 (2003).

32 R. M. Alosmanov, A. A. Azizov, A. M. Maharramov, Russ. J. Gen. Chem. 2011, **81**, 7.

33 M. M. Rafi, K. S. Z. Ahmed, K. P. Nazeer, D. S. Kumar, M. Thamilselvan, Appl. Nanosci. 2015, DOI 10.1007/s13204-014-0344-z

34 J. Rouquerol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. M. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing, and K. K. Unger, Pure Appl. Chem., 1994, **66**, 1739.

35 L. O. dos Santos and V. A. Lemos, Water Air Soil Pollut., 2014, **225**, 2086.

36 F. A. Aydin and M. Soylak, Talanta, 2007, **72**, 187.

37 J. G. Chen, H. W. Chen, S. H. Chen, L. Lin, Y. Y. Zhong, Chem. Res. Chinese U., 2007, **23**, 143.

38 M. Soylak and L. Elci, J. Trace Microprobe Tech., 2000, **18**, 397.

39 M. Rezvani, H. Ebrahimzadeh, A. Aliakbari, A. Khalilzadeh, M. Kasaeian and M. M. Amini, J. Sep. Sci., 2014, **37**, 2559.

40 A. Samadi and M. Amjadi, Microchim. Acta, 2015, **182,** 257.

41 G.H. Mirzabe and A.R. Keshtkar, J. Radioanal. Nucl. Chem., 2015, **303**,561.

42 H. Tavallali, G. Deilamy-Rad and H. Ansari, Iran. J. Anal. Chem., 2014, **1,** 87.

43 H. Shirkhanloo, A. Khaligh, H. Zavvar Mousavi and A. Rashidi Int. J. Environ. Anal. Ch., 2015, **95**, 16.

44 V.N. Bulut, M. Tufekci, C. Duran, M. Soylak and H. Kantekin, Clean, 2010, **38,** 678.

45 T. Li and J. Yang, J. Iran. Chem. Soc., 2015, **12,** 367.

46 A. Gundogdu, D. Ozdes, C. Duran, V.N. Bulut, M. Soylak and H.B. Senturk, Chem. Eng. J., 2009, **153,** 62.

47 H.Z. Mousavi and J. Derakhshankhah, J. AOAC Int., 2014, **97,** 1707.

48 S. Baytak and A.R. Turker, Turk J. Chem., 2004, **28,** 243.

49 M. Hossein, N. Dalali, and A. Karimi, Turk J. Chem., 2010, **34,** 805.

50 H. B. Senturk, A. Gundogdu, V. N. Bulut, C. Duran, M. Soylak, L. Elci and M. Tufekci, J. Hazard. Mater., 2007, **149**, 317.

51 E. Yilmaz and M. Soylak, Talanta., 2013, **116**, 882.

52 S. Saracoglu, M. Soylak, L. Elci, Can. J. Anal. Sci. Spectrosc., 2001, **46,** 123.

Figure captions

Fig. 1. The FT-IR spectra of the phosphorus-containing polymeric sorbent (PhCPS) and magnetic phosphorus-containing polymeric sorbent (M-PhCP).

Fig. 2. SEM images of the phosphorus-containing polymeric sorbent (PhCPS) (A) and magnetic phosphorus-containing polymeric sorbent (M-PhCP) (B).

Fig. 3. Elemental mapping image (EMI) of the magnetic phosphorus-containing polymer

Fig. 4. EDX spectrum of magnetic phosphorus-containing polymer

Fig. 5. XRD pattern of the phosphorus-containing polymer (A) and magnetic phosphorus-containing polymer (B)

Fig. 6. Nitrogen adsorption/desorption isotherm of the magnetic phosphorus-containing polymeric sorbent (M-PhCP).

Fig. 7. Effect of pH on the recoveries of Pb(II) and Cd(II) (N (number of samples analyzed)=3, amount of analytes : 20 µg lead(II) and 10 µg cadmium(II), amount of adsorbent: 100 mg, amount of ligand: 0.1 mg, eluent: 5 mL, 0.5 mol L^{-1} of HNO_3 in acetone).

Fig. 8. Effect of the amount of ligand on the recoveries of Pb(II) and Cd(II) (N=3, amount of analytes : 20 µg lead(II) and 10 µg cadmium(II), pH: 6.0, amount of adsorbent: 100 mg, eluent: 5 mL, 0.5 mol L^{-1} of HNO_3 in acetone).

Table 1. Effects of various eluents on the recoveries of Pb(II) and Cd(II) (N=3, Amount of analytes : 20 µg lead(II) and 10 µg cadmium(II), pH: 6.0, Amount of adsorbent: 100 mg).

	Recovery, %	
Eluent Type	**Pb(II)**	**Cd(II)**
7 mL 0.05 mol L^{-1} HNO_3 in Acetone	77±1	69±4
7 mL 0.1 mol L^{-1} HNO_3 in Acetone	73±6	69±3
7 mL 0.25 mol L^{-1} HNO_3 in Acetone	70±10	46±2
7 mL 0.5 mol L^{-1} HNO_3 in Acetone	95±2	99±2
1 mL 0.5 mol L^{-1} HNO_3 in Acetone	44±0	50±0
2 mL 0.5 mol L^{-1} HNO_3 in Acetone	67±0	45±1
3 mL 0.5 mol L^{-1} HNO_3 in Acetone	104±6	45±0
4 mL 0.5 mol L^{-1} HNO_3 in Acetone	89±2	45±0
5 mL 0.5 mol L^{-1} HNO_3 in Acetone	95±2	101±3

N: number of samples analyzed

Table 2. Influences of interfering species on the recoveries of Pb(II) and Cd(II) (N=3, Amount of analytes : 20 µg lead(II) and 10 µg cadmium(II), pH= 6.0, amount of ligand= 0.1 mg, sample volume: 20 mL, eluent: 5 mL, 0.5 mol L^{-1} of HNO_3 in acetone).

			Recovery, %	
Ions	**Concentration, µg/ml**	**Added as**	**Pb(II)**	**Cd(II)**
Na^+	10000	$NaNO_3$	100±0	99±2
K^+	10000	KCl	95±4	97±1
Co^{2+}	25	$Co(NO_3)_2.6H_2O$	98±5	101±1
Cu^{2+}	25	$Cu(NO_3)_2.3H_2O$	95±2	99±2
Zn^{2+}	25	$Zn(NO_3)_2.6H_2O$	97±2	101±3
Fe^{3+}	25	$Fe(NO_3)_3.9H_2O$	96±0	102±2
Mn^{2+}	25	$Mn(NO_3)_2.4H_2O$	95±2	100±1
Cd^{2+}	25	$Cd(NO_3)_2.4H_2O$	99±5	-
Ni^{2+}	25	$Ni(NO_3)_2.6H_2O$	100±4	103±1
Pb^{2+}	25	$Pb(NO_3)_2.6H_2O$	-	99±2
Cr^{3+}	25	$Cr(NO_3)_3.9H_2O$	100±4	97±2
Cl^-	10000	KCl	95±4	97±1
SO_4^{2-}	5000	Na_2SO_4	98±3	96±6

Table 3. Determination of lead and cadmium in certified reference materials (N=3, pH= 6.0, amount of ligand= 0.1 mg, sample volume: 20 mL, eluent: 5 mL, 0.5 mol L^{-1} of HNO_3 in acetone).

Certified Reference Material	Analyte	Found, µg L^{-1}	Certified Value, µg L^{-1}	Recovery, %
TMDA- 64.2 Fortified Water	Pb	280±27	288	97
	Cd	266±6	266	100
SPS-WW2 Waste water	Pb	513±1	500	103
	Cd	103±5	100	103

Table 4. Addition-Recovery tests for river water, dam water, well water and waste water, (N=3, pH= 6.0, amount of ligand= 0.1 mg, sample volume: 20 mL, eluent: 10 mL, 0.5 mol L^{-1} of HNO$_3$ in acetone).

		Pb(II)		Cd(II)	
Sample	Added, µg L^{-1}	Found, µg L^{-1}	Recovery, %	Found, µg L^{-1}	Recovery, %
River water	0	52±6	-	LOD	
	40	93±9	101	41±0	103
Dam water	0	LOD	-	LOD	-
	133	133±0	100	141±0	106
Well water	0	45±0	-	45±0	-
	133	178±0	100	178±0	100
Waste water	0	158±31	-	18±0	-
	200	347±9	97	214±5	98

[a] BDL: Below the detection limit.

[b] Mean ±standard deviation.

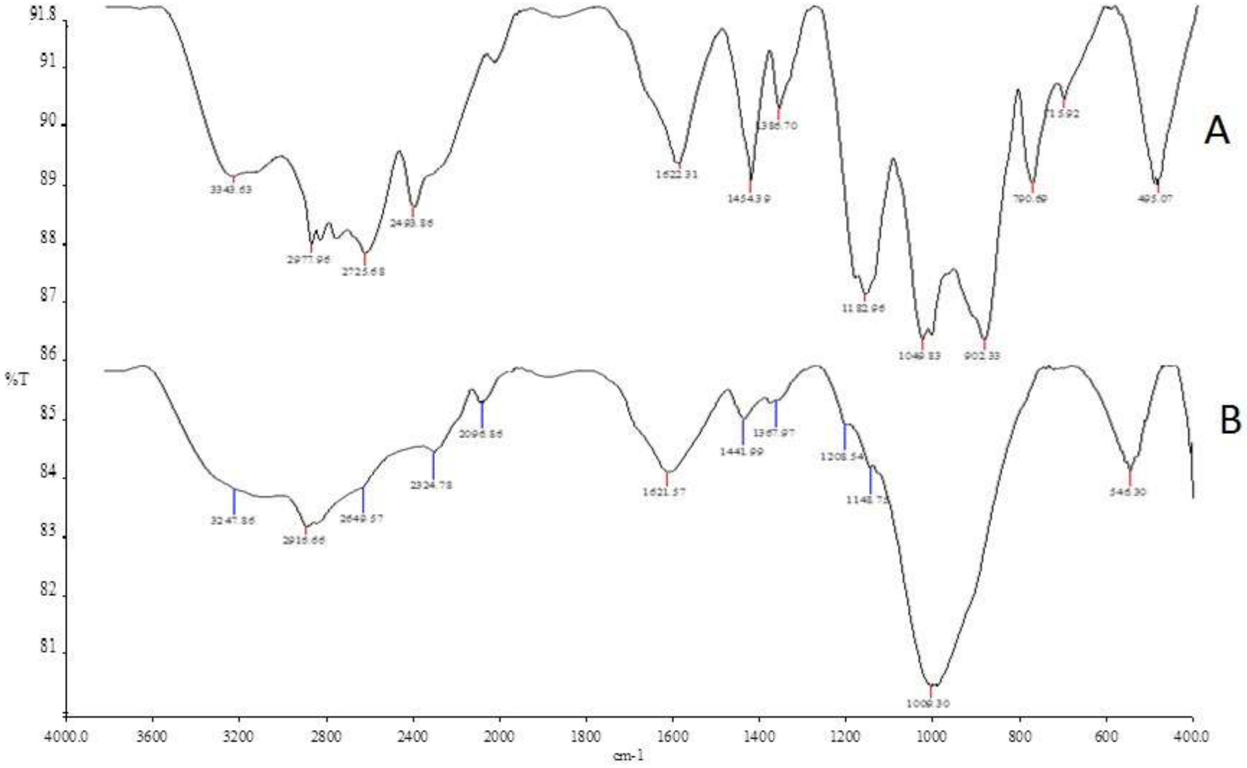
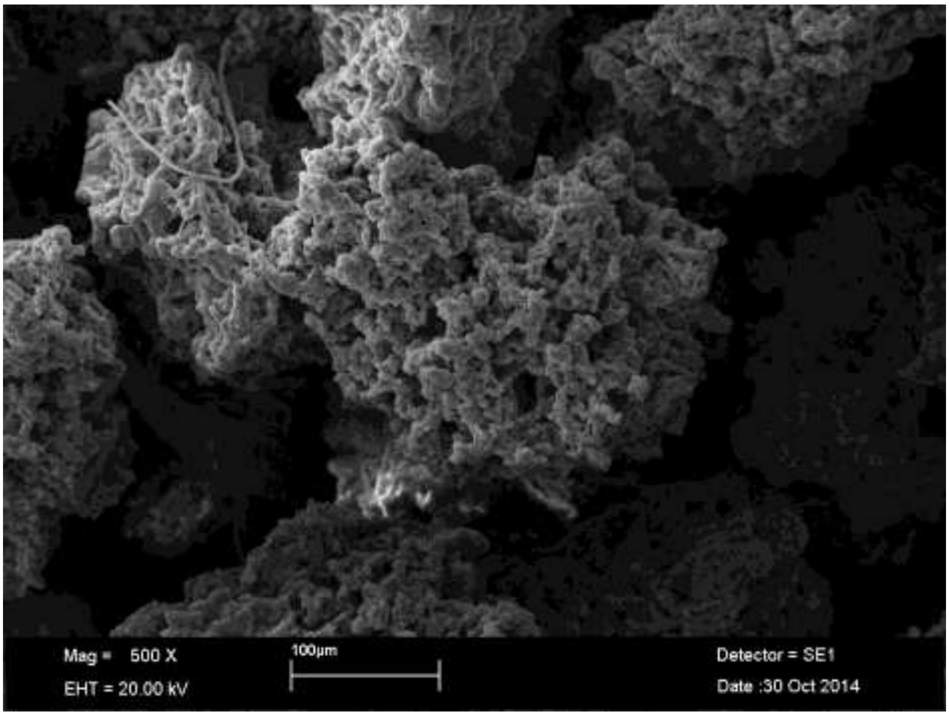
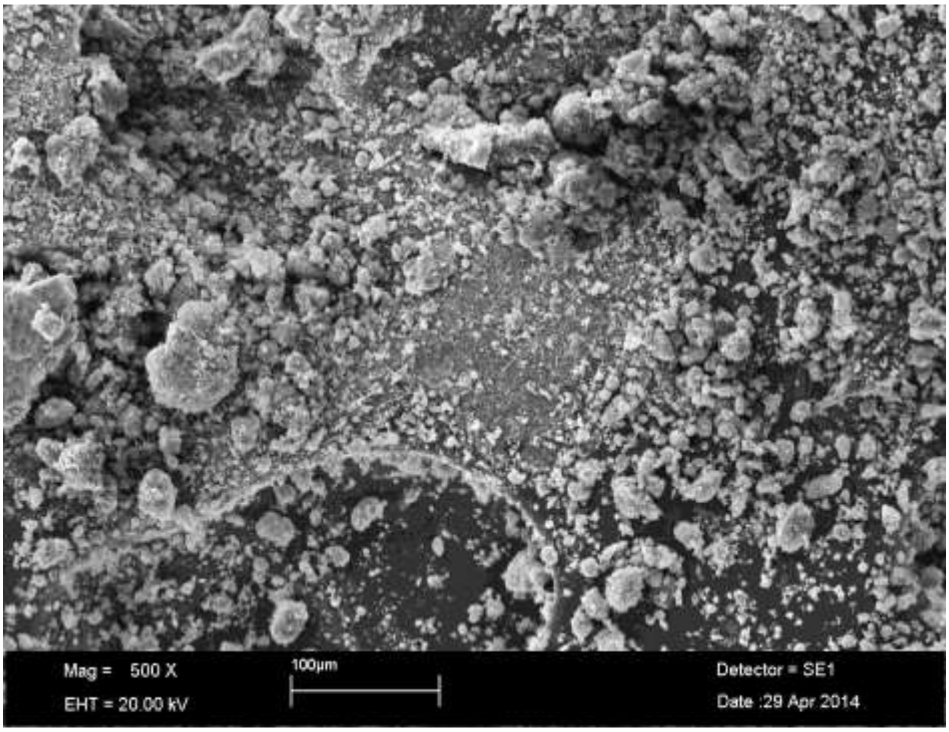

91.8
91
90
89
88
87
86
85
84
83
82
81
%T
3343.63
2977.96
2725.68
2493.86
1622.31
1454.39
1386.70
1182.96
1049.83
902.33
790.69
715.92
495.07
A
3247.86
2916.66
2649.57
2324.78
2096.86
1621.57
1441.99
1367.97
1208.54
1148.75
1009.30
546.30
B
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1

Fig. 1.



(A)



(B)

Fig. 2.

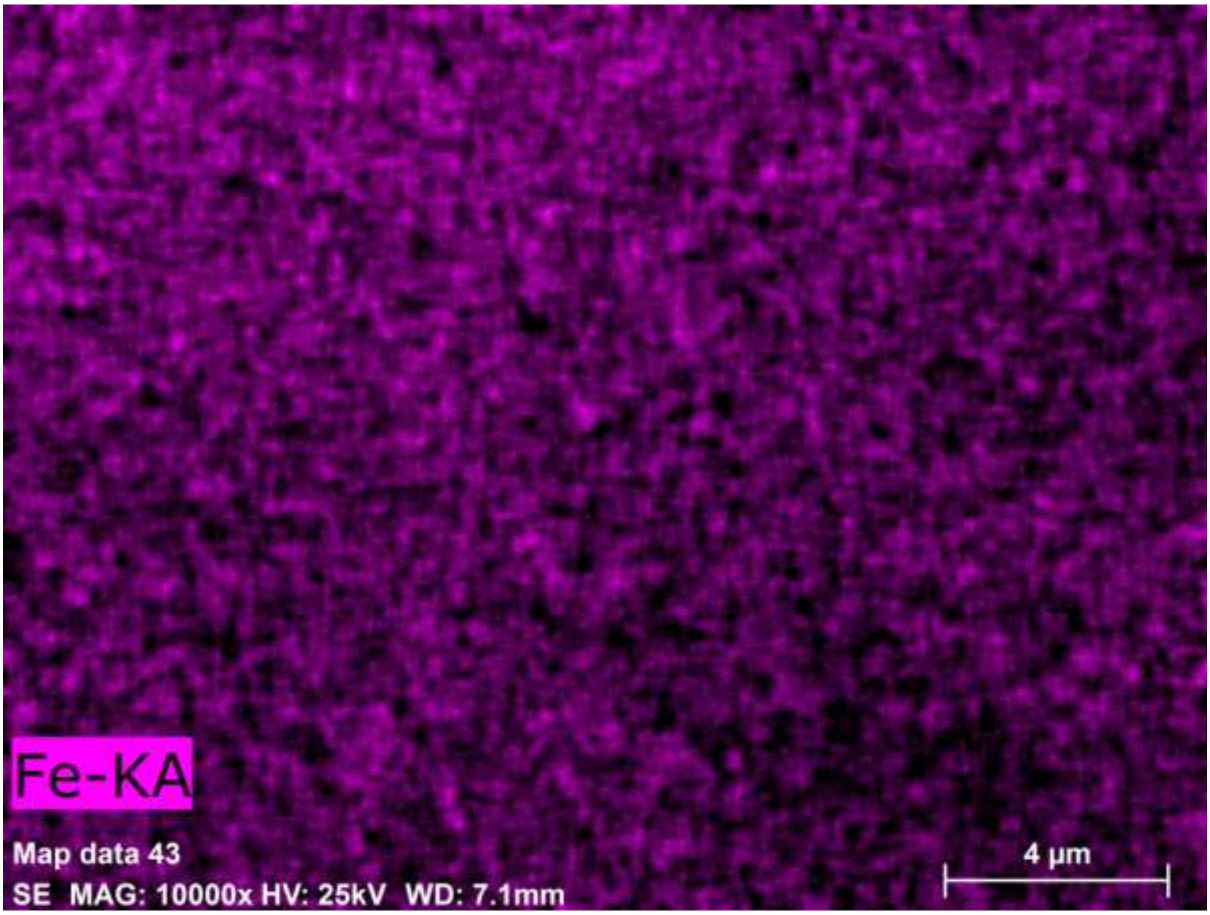


Fig. 3.

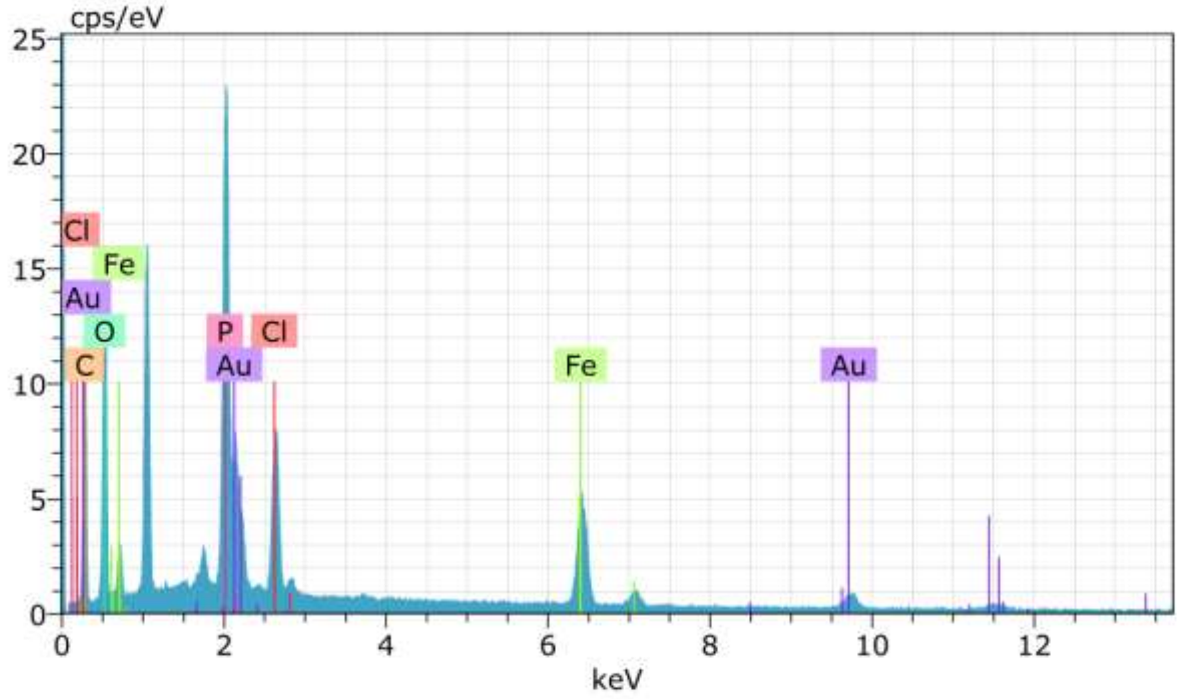


Fig. 4.

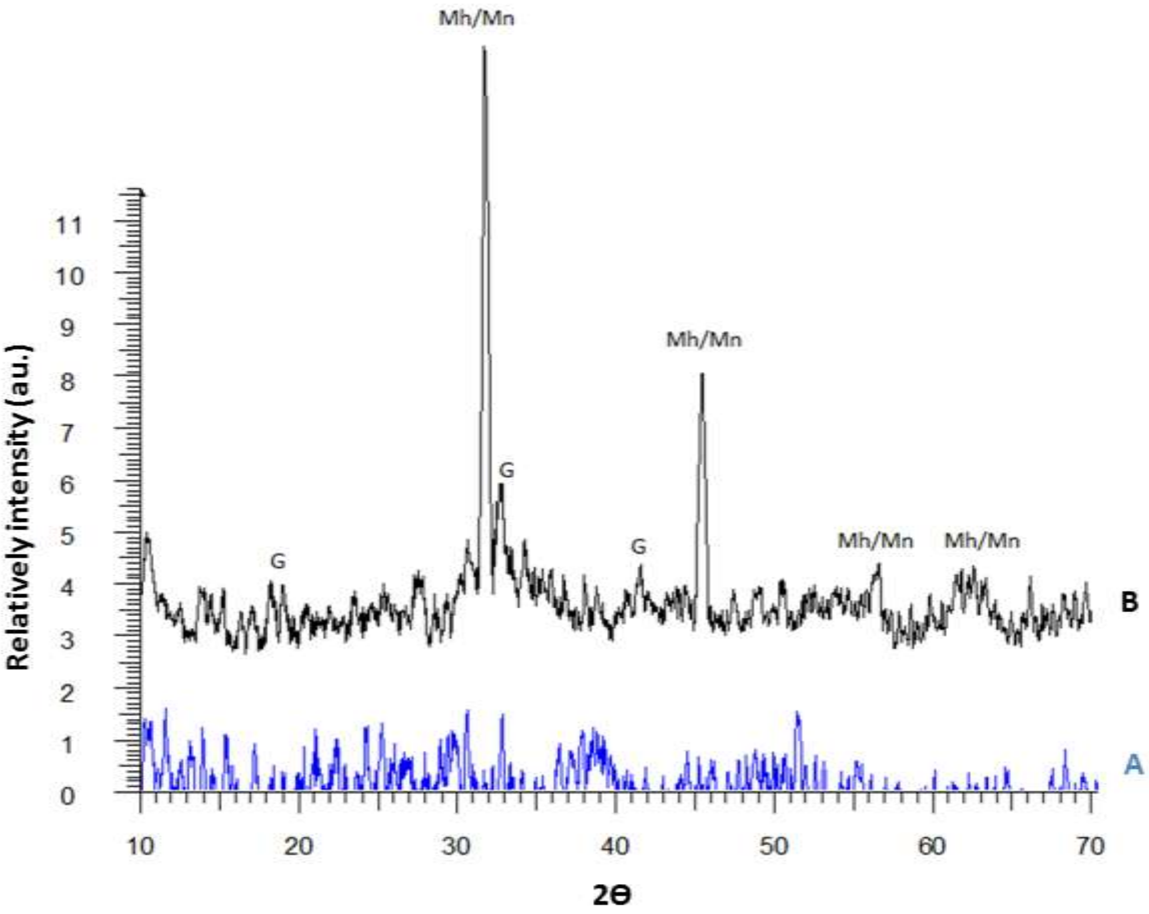

Mh/Mn
Mh/Mn
G
G
G
Mh/Mn
Mh/Mn
B
A
Relatively intensity (au.)
0
1
2
3
4
5
6
7
8
9
10
11
10
20
30
40
50
60
70
2Θ

Fig. 5.

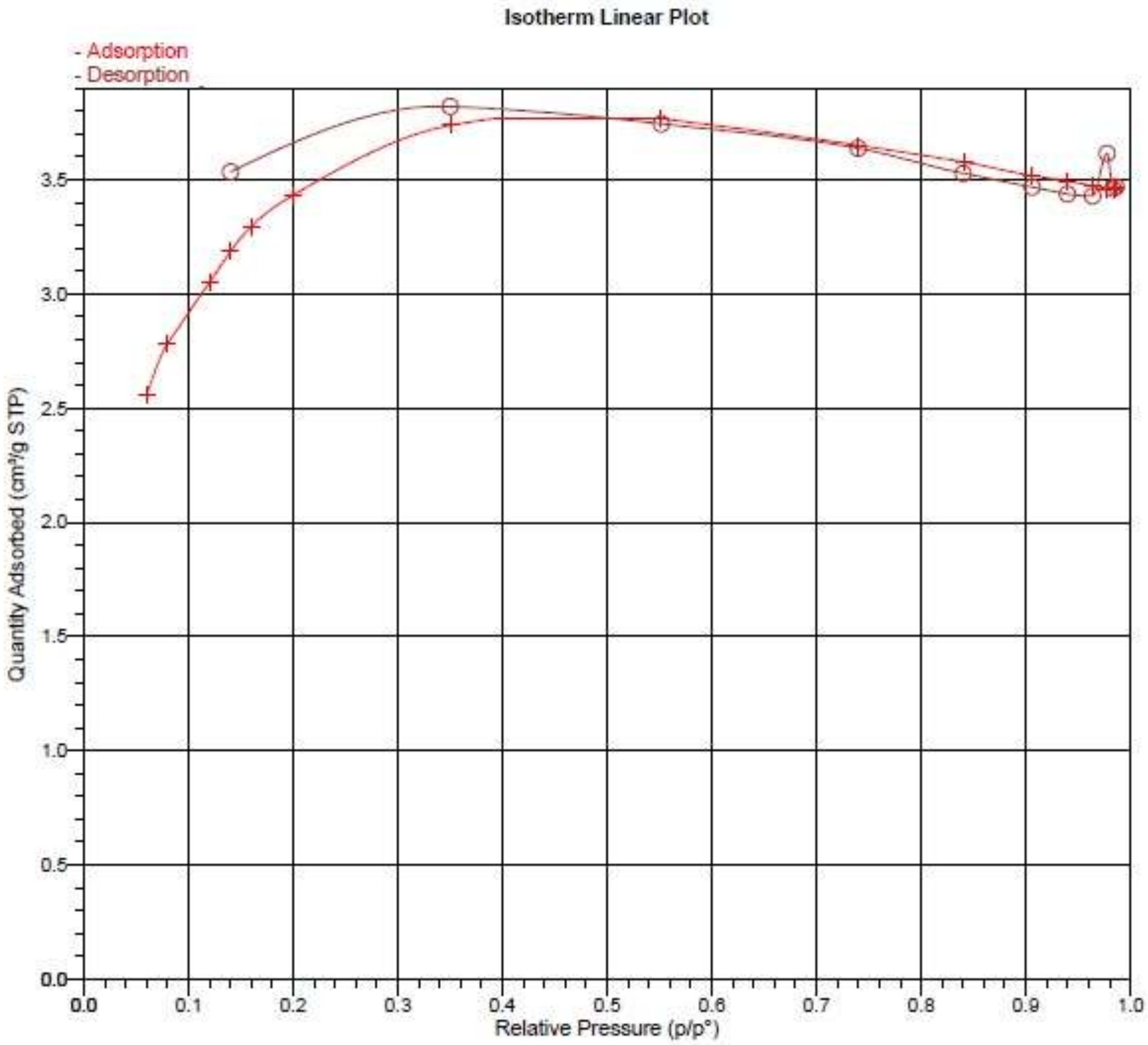

Isotherm Linear Plot
- Adsorption
- Desorption
Quantity Adsorbed (cm³/g STP)
Relative Pressure (p/p°)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Fig. 6.

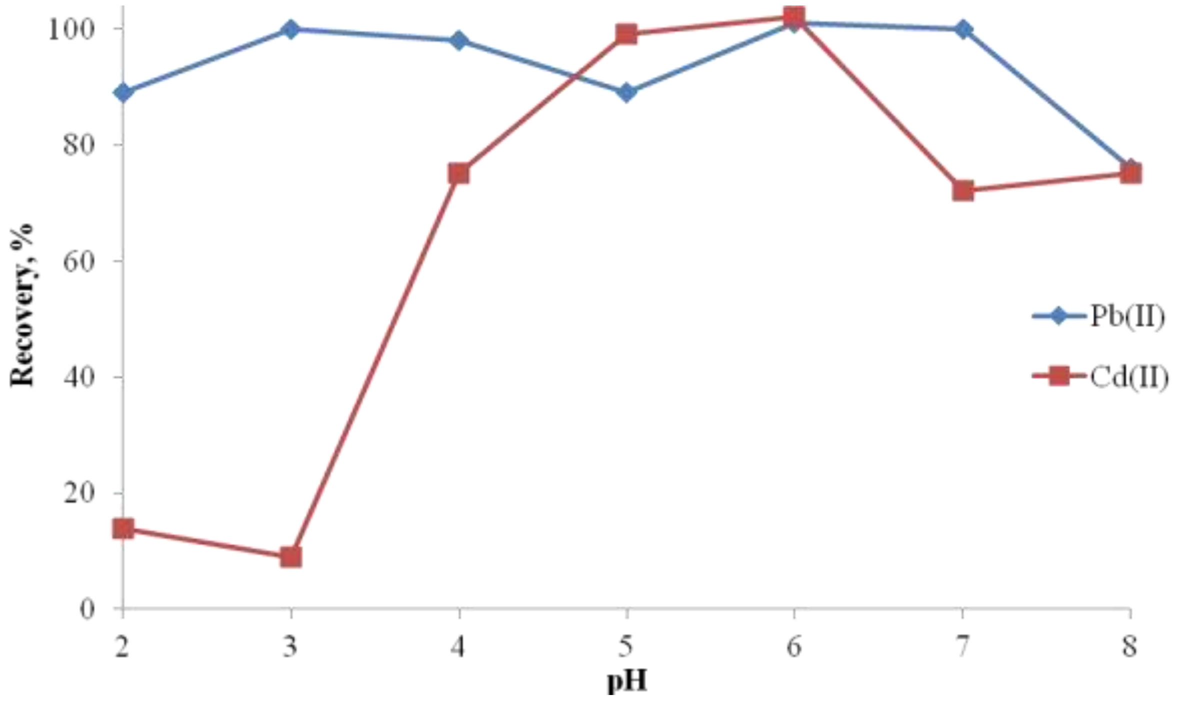


Fig. 7.

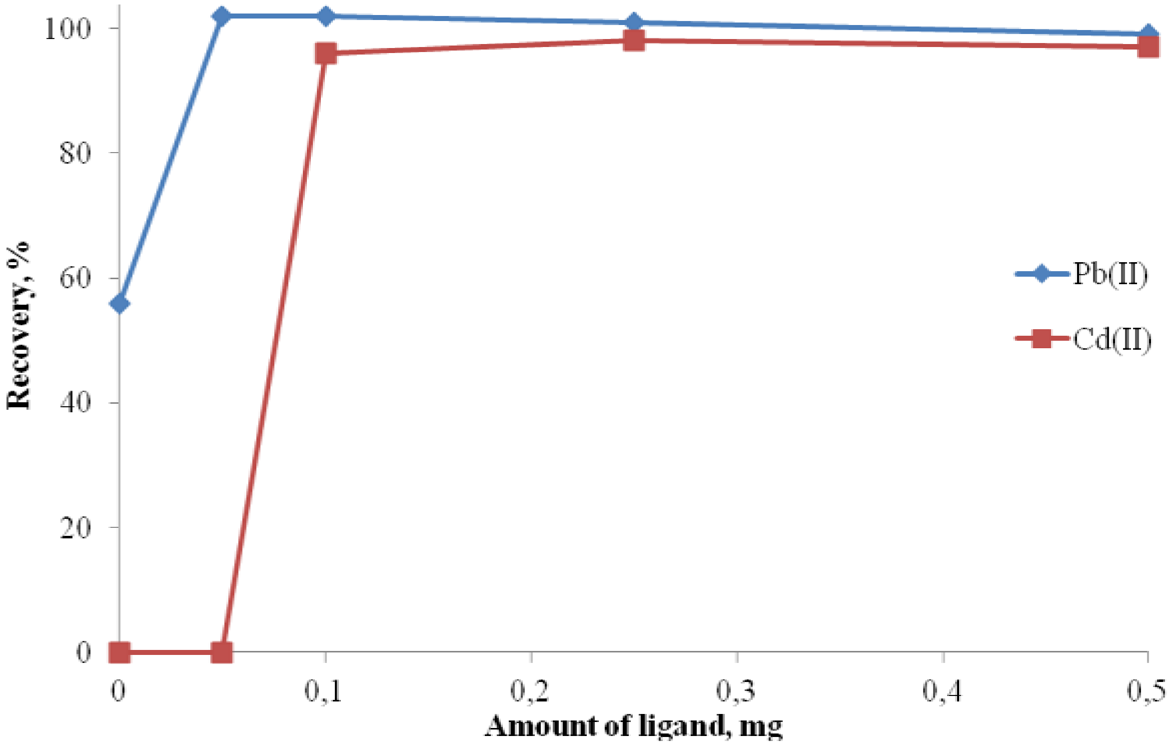

100
80
60
40
20
0
Recovery, %
0
0,1
0,2
0,3
0,4
0,5
Amount of ligand, mg
Pb(II)
Cd(II)

Fig. 8.