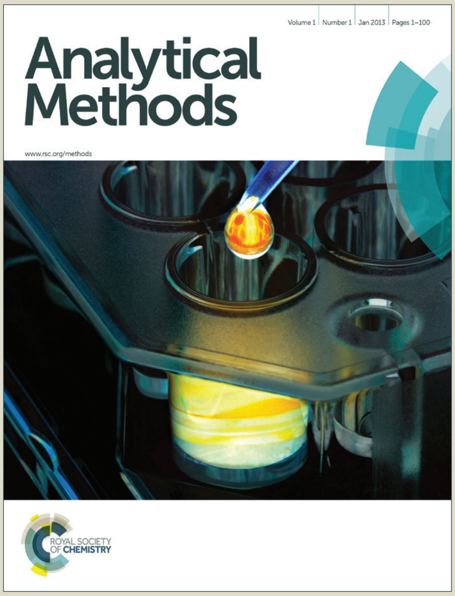
Analytical Methods

Accepted Manuscript



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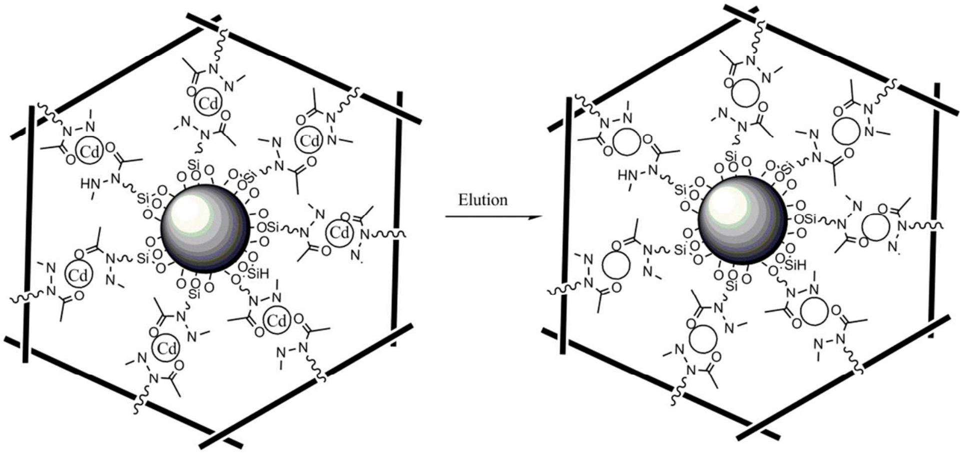
Graphical Abstract: A schematic diagram for cadmium ion imprinted polymer



New magnetic polymeric nanoparticles for extraction of trace cadmium ions; determination of cadmium content in diesel oil samples

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Abstract

A novel highly selective magnetic sorbent was synthesized for rapid preconcentration of Cd(II) ions. A cadmium-imprinted polymer was grafted on Fe_3O_4 nanoparticles to give the magnetic property to the sorbent. The grafting was characterized by IR spectroscopy, XRD patterns, scanning electron microscopy and differential thermal analysis. The effects of sample pH, eluent factors (type, concentration and volume) and the time of adsorption and desorption were investigated. The retained cadmium determination was performed by flame atomic absorption Spectroscopy. The limit of detection and relative standard deviation values were 0.09 µg L^{-1} and 1.7 %, respectively, under optimum conditions. The accuracy of the method was confirmed using standard materials. Finally, it was applied to the determination of Cd(II) in used and non-used diesel oils.

Keywords: Cadmium determination; Magnetic nano-particles; Ion imprinted polymer

1. **Introduction**

Cadmium is one of the most toxic heavy metals in the environment, even in low concentrations.[1] It inters human body through food chain and the accumulation in the human organs is more serious than other creatures.[2] Cd (II) can cause some devastating health problems such as subversion of nervous system, stomachache, vomiting, decrease of safety, cell damage and cancer.[3] In this regard, the world health organization (WHO) recommended a maximum of 3 ppb Cd (II) in their guidelines for drinking water quality.[4] Therefore, extraction, pre concentration and determination of trace cadmium in samples that are influencing our environment are of a great importance and need a special attention. Many spectrophotometric techniques such as Inductively Coupled Plasma-Mass Spectrometry (ICP-MS),[5-6] Atomic Absorption Spectrometry (AAS)[7-8] and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)[9] have been applied for quantitative and qualitative determination and separation of Cd (II) in complex matrixes. Among the methods, Flame Atomic Absorption Spectrometry (FAAS) has become a standard analytical tool for determination of various heavy metals due to its advantages such as simplicity in operation and low cost of analysis[10].

Despite the advantages of the technique, this method has also some disadvantages such as higher limit of detection (LOD) than the usual concentrations in real samples, and the matrix interfering effects of the working media.[11] These reasons make it essential to have a preconcentration step prior to the main determination by FAAS. Different preconcentration methods like Cloud Point Extraction (CPE),[12] coprecipitation,[13] liquid phase micro extraction,[14] Liquid–Liquid Extraction (LLE),[15] Solid–Liquid Extraction (SLE)[16] and Solid-Phase Extraction (SPE)[17-18] have been used for the enrichment of cadmium. One of widely used and fast emerging pre-concentrative separation techniques for this purpose is SPE due to the following advantages. These include higher enrichment factors, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of reagents, flexibility, and ease of automation.[19-20] Various sorbets such as silica gel,[21] chelating fibers[22] and chelating resins,[23] etc, have been reported as solid phases. However these sorbents still suffer from lack of selectivity.[24]

Ion imprinting technique is a powerful tool for preparing high selective sorbent used for extraction and preconcentration of variety of ions. The high selectivity of ion Imprinted Polymers (IIP) arises from the specificity of interaction between the ligand which is present in the polymer pores' surface, with the metal ions.[25-29] The coordination number, the charge, and the size of the metal ions are some factors used for selective removal, separation, pre concentration and extraction of the target metal ions.[30] However low surface area and difficulty in separation, are the failures of these polymers as a sorbent in SPE.[31] The magnetic properties of Fe_3O_4 nanoparticles makes this oxide capable of being collected easily by a magnet; in addition, this material has high thermal and mechanical stability (decreased susceptibility to swelling and shrinking) and high surface area (up to 400 m^2g^{-1}).[32] These merits make the nanoparticles a suitable support, to be grafted by IIP so that we could gain a magnetic sorbent with high efficiency in extraction due to the high active surface area and high selectivity.[33]

In this study, a new Cd (II)-imprinted polymer was grafted on Fe_3o_4 nanoparticles as a new sorbent for selective removal of trace Cd (II) from aqueous solutions. The kinetics (adsorption and desorption time), maximum capacity and selectivity of this new sorbents for Cd (II), beside other figures of merit, were investigated . Finally the method was successfully applied for determination of Cd (II) in diesel oil samples after extraction induct by emulsion breaking (EIEB).

2. Experimental

2.1. Apparatus

IR spectra were recorded by a BOMEM/MB series spectrometer. X-ray diffraction patterns were obtained on a STOE diffractometer with Cu K_α radiation. Thermal gravimetric and differential thermal analysis (TG/DTA) was carried out on a Bahr STA-503 instrument under air atmosphere. The elemental analysis was performed with a Thermo Finnigan Flash-2000 microanalyzer (Italy). Cadmium concentrations were determined by an AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer in an air-acetylene flame, according to the user's manual, provided by the manufacturer. A cadmium hollow cathode lamp was used as the radiation source with a wavelength of 228.8 nm. All pH measurements were performed at 25 ± 1 °C with a digital WTW Metrohm 827 Ion Analyzer (Herisau, Switzerland), equipped with a combined glass-calomel electrode. Magnetic separation was carried out by a super magnet with 1.4 Tesla magnetic field (10 × 5 × 4 cm). Morphology of particles was observed on a Philips XL-30 scanning electron microscope (SEM). Specific surface area was measured by nitrogen adsorption technique using a Micrometitis ASPS 2010 analyzer.

2.2. Reagents and materials

All reagents used were of the analytical grade and were used without further purification. A 1000 µg mL^{-1} standard solution of Cd (II) was purchased from Aldrich Company. HCl, HNO_3, $HClO_4$, H_2SO_4, $Na_3C_3H_5O(CO_2)_3$, Na_2HPO4, NaH_2PO_4, CH_3COOH, $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ were purchased from Merck Company (http://merck.de) (Darmstadt, Germany). Ethylene glycol dimethacrylate (EGDMA) was obtained from Fluka Company (Buchs, Switzerland). 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Acros Organics Company (New Jersey, USA).

The working solutions of Cd (II) were obtained by diluting the standard solution with buffer, and pH adjustments were also performed with the appropriate buffer solutions. For pH of 3 to 4, a mixture of $Na_3C_3H_5O(CO_2)_3$/ HCl (trisodium citrate/hydrochloric acid) was used. A solution of CH_3COOH/ $NaCH_3COO$ was used to adjust pH 4-6, while a buffer solution containing Na_2HPO_4/ NaH_2PO_4 was used for pH 6-8. All the required solutions were prepared using deionized water provided by a Milli-Q (Millipore, Bedford, MA, USA) purification system. Standard material samples (NIST 1571 and NIST 1572) with certified cadmium content were obtained from National Institute of Standards and Technology.

2.3. Preparation of Fe_3O_4 nano particles

Fe_3O_4 nano particles were synthesized according to previously reported method.[34] Briefly, 10.4 g of $FeCl_3.6H_2O$ and 4.0 g of $FeCl_2.4H_2O$ were dissolved in 100 mL of deionized water, degassed with nitrogen gas for 15 min and heated to 80 ºC. Then, 15 mL of NH_4OH (32% solution) was added dropwise to the solution. After 15 min, the solid was separated by a magnet and washed three times with 0.1 mol L^{-1} NaCl solution. The formation of nanoparticles was confirmed by IR spectroscopy and X-ray powder diffraction. Single point BET analysis showed a surface area of 317 m^2 g^{-1} for Fe_3O_4 nanoparticle.

2.4. Preparation of vinyl functionalized Fe_3O_4

Vinyl functionalization of Fe_3O_4 NPs was performed by the reaction of silan agents with Fe_3O_4 NPs according to our recent report.[35] In this approach, 1.0 g of prepared Fe_3O_4 NPs was suspended in 50 mL of toluene, afterward 2.0 mL of 3-vinyletriethoxy silane was added to the solution and the mixture was stirred for 24 h. The solid-phase was separated from the solvent by a magnet and washed 3 times with 50 mL of ethanol and then dried at room temperature. The vinyl functionalization of Fe_3O_4 NPs was confirmed by IR spectroscopy and elemental analysis. Elemental analysis shows 0.69 mmol g^{-1} vinyl coated on this sorbent (C=2.47 %, H=0.34%).

2.5. Preparation of magnetic Cd (II)-IIP nano particles

In order to prepare Cd (II) imprinted polymer, firstly, the required ligand was synthesized through following process. 1 mmol (4-chlorobenzohydrazide) was added to vinyl chloride (1 mmol) in 50 mL methanol and triethylamine mixture (1:1, V:V), and then stirred for 24 h. Afterward, in order to prepare the cadmium complex, 1 mmol of Cd (II) and 1 mmol of the prepared ligand were mixed with methanol and stirred for 1 h in order to complete the complexation reaction. The vinyl functionalized Fe_3O_4 NPs were then mixed with the solution followed by adding 1 mL EGDMA, as cross-linking agent, and purging N_2 gas for 10 min to remove oxygen from the reaction mixture. Then 0.38 g AIBN, as initiator, was added and polymerization reaction was carried out in the oil bath at 70 ºC for 24 h. The synthesized polymer was firstly washed with distilled water and then with optimized eluent (4 mL of 0.1 M $HClO_4$ solution), in order to remove the cadmium ions and make the sorbent ready for extraction. In order to confirm the removal of cadmium ions, the amount of Cd(II) was determined by FAAS after treatment with piranha solution (H_2SO_4+H_2O_2). Piranha solution dissolves the organic parts of these particles and releases Cd(II) ions in solution, which can be determined by FAAS. This sorbent was characterized by XRD pattern, IR spectroscopy, thermal analysis and SEM micrograph. A schematic diagram for this synthesis is represented in Fig. 1.

2.6. Extraction process

50 mL of aqueous solution containing Cd (II) is equilibrated with 0.05 g of the magnetic Cd-IIP nano particles for 4 min shaking. Then the sorbent containing retained ions, is collected with a super magnet and subsequently the ions are eluted with 4 mL of 0.1 M $HClO_4$ solution. The Cd (II) ions in the elution solution are then determined by FAAS. The used IIP could be reused for the next experiments after washing with the optimized eluent.

2.7. Standard reference materials digestion

Standard reference materials were digested with 6 mL of HCl (37%) and 2 mL of HNO_3 (65%) in a microwave digestion system. Digestions were carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W and then vented for 8 min. Afterward, the residues of digestion were diluted with deionized water.

2.8. Diesel oil extraction as a real sample

The cadmium ions in the used and un-used diesel oil were extracted through an extraction induct by emulsion breaking (EIEB) according to previously reported paper.[36] According to this method, the oil was mixed with acidic triton X-100 solution in a capped plastic tube and stirred vigorously. After formation of emulsion, the tube was transferred to the temperature-controlled water bath kept at the temperature 75 ºC and it was heated until the emulsion breaking. The result of the emulsion breaking was three well separated phases, among which the acidic aqueous phase contains the extracted metals. The proposed enrichment method was used for selective determination of Cd (II) in the aqueous phase of used and un-used diesel oil.

3. Result and discussion

3.1. Sorbent characterization

Formation of Fe_3O_4 NPs was confirmed by X-ray powder diffraction. Single point BET analysis showed 317 m^2 g^{-1} specific area for synthesized Fe_3O_4 nano-particles. Modification of these particles with vinyl groups was performed by direct method for functionalization of Fe_3O_4 with triethoxysilan agents.[31]. The reaction of vinyl functionalized Fe_3O_4 as a monomer with cadmium complex as another monomer in presence of an initiator (AIBN) and EGDMA as cross linking agent cause formation of this sorbent. A schematic diagram of the synthesis route is shown in Fig. 1. Formation of this magnetic ion imprinted polymer was confirmed by IR spectroscopy, high-angle X-ray powder diffraction, SEM micrograph and thermal analysis. The C-H aromatic, C-H aliphatic, C=O, C=N and C=C vibrations were appear in IR spectrum at 3021, 2919, 1738, 1639 and 1633 cm^{-1}.

In order to investigate the presence of Fe_3O_4 in the structure of polymer, the XRD pattern of this composite was recorded (Fig. 2). According to the XRD pattern, the Fe_3O_4 structure has been remained unchanged after functionalization. On the other word the Fe_3O_4 was not decomposed and did not convert to Fe_2O_3. The average crystallite size of IIP nanoparticles was estimated from the XRD pattern using Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where D is the average crystallite size, λ is the X-ray wavelength (1.5406 Å), β is the full-width at half maximum (FWHM) and θ is the diffraction angle. Here K = 0.9 is for spherical shape. So the crystallite size of IIP nanoparticles was computed from XRD pattern and found to be about

61 nm. According to this analysis, it could be concluded that the size of particles are in the range of nanometer.

For further investigation of the size and morphology of the synthesized sorbent, the SEM micrograph of this sorbent was recorded. According to the SEM micrograph, the particles had approximately 60 nm diameter and the morphology is spherical (Fig. 3).

In order to investigate the thermal stability of this sorbent, the TGA/DTA analysis was recorded under air atmosphere. As the curves in Fig. 4 show, this magnetic sorbent is stable up to 200 °C and about 23 % of this sorbent is polymer.

3.2. Optimization of parameters

In order to achieve the best performance, the separation/preconcentration procedure and the effective factors such as pH of the sample solution, type, concentration and volume of eluent, desorption and desorption time and maximum adsorption capacity were optimized. Different important figures of merit such as selectivity of the magnetic Cd (II)-IIP nano particles, LOD and recovery were also investigated.

3.2.1 Effect of pH

The effect of variety of pH values on Cd (II) adsorption was investigated using batch procedure. For this purpose, pH of sample solutions was adjusted to pH 3-8 and the extraction procedure was applied on these solutions. 0.01 g polymer was added to 20 mL of 5 mg L^{-1} solutions of Cd(II) with different pHs. After following the amount of cadmium ions in eluent by FAAS, it was revealed that he best pH of adsorption is 7. This fact can be explained as follow. In low pHs, the active sites of the ligands are protonated and are not able to coordinate to the cadmium ion anymore, which decrease the recovery. In high pHs, the cadmium ions turn to cadmium hydroxyl and do not retain on the sorbent anymore and as consequence the recovery decreases. The results of the experiment can be seen in Fig. 5.

3.2.2 Sorption time

Since the short analysis time reduces the analytical efficiency and the long analysis times are not desired, optimizing the sorption time is essential. In order to study the effect of adsorption time, 0.01 g of polymer was added to 20 mL of 5 mg L^{-1} solution of Cd(II) and the extraction procedure was performed in different time durations(1, 2, 3, 4, 5 min). Then sorbents were isolated by placing a magnet and the pre concentrated analytes in eluents were determined by FAAS. As the results show in Fig. 6, the optimum adsorption time was found to be 4 min.

3.2.3 Type, concentration and volume of eluent

In order to obtain the most efficient removal of the ions from the sorbent, type, concentration and volume of eluent solution were optimized. Different acids including $HClO_4$, HNO_3, HCl, H_2SO_4 were tested for desorption of Cd (II) ions. For this purpose, after adsorption of Cd (II) ions according to mentioned procedure, the sorbent was isolated by placing a magnet and suspended in 10 mL of each acid. After eluting the adsorbed ions with different acids and also their different concentrations, the Cd (II) content of each eluent was measured by FAAS. The results (Table 1) showed that 0.01 M $HClO_4$ led to the most efficient and complete elution. Finally the elution tests were done in different volumes of 0.01 M $HClO_4$. The results showed that the optimum volume of the eluent was also revealed to be 4 mL.

3.2.4 Desorption time

In this study, time of desorption of the retained Cd (II) ions, was studied through a batch experiment. For this purpose, 4 mL of eluent was added to 0.01g of the sorbent and the mixture was shaken. This experiment was performed with different shaking times: 5, 10, 15, 20, 25, 30, 40, 50 and 60 min. After determination of eluted cadmium ions by FAAS, as it can be seen in the Fig. 7, the most efficient adsorption time was found to be 50 min.

3.3. Maximum adsorption Capacity

In order to determine the sorbent maximum capacity, 0.01 g of prepared polymer was added to 10 mg solution of Cd (II) (pH=7). After shaking for 4 min and collecting the sorbent by the magnet, the cadmium ions in the elution solution were determined by FAAS. The maximum adsorption capacity was found to be 52.6 mg g^{-1} (0.47 mmol g^{-1}).

3.4. Selectivity of the magnetic Cd (II) IIP against other cations

Effect of a variety of cations usually found in natural samples, on the determination of Cd (II) was studied. As their chloride salts, various concentrations of Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+} and Cr^{3+} were added to individual cadmium-containing solutions listed in Table 2. As shown in Table 2, the vast majority of transition metals do not interfere the concentrations encountered in nature, and the method is selective toward cadmium extraction at pH=7. Furthermore, extraction was not affected by high concentrations of alkaline and alkaline earth metals. This high selectivity could be because of imprinting technique, which produces very selective sites that are Cd(II) ions size and attract the ions only. Also the imprinting factor was evaluated. The imprinting factor (IF) is defined as:

$$\mathrm{IF} = \frac{B_{IIP}}{\mathrm{B_{NIP}}}$$

where B_{IIP} and B_{NIP} depict the binding capacity of the ion imprinted polymer and the non-imprinted polymer, respectively. According to this equation the IF was 3.1.

3.5. Figures of merit

In order to determine the limit of detection (LOD) of the presented method, adsorption procedure was performed using 500 mL blank solution (n=10) under optimal experimental conditions. LOD value for cadmium ions on the magnetic sorbent was determined to be 0.09 ng mL^{-1}. The results were obtained from the relationship expressing $C_{LOD} = 3S_b/m$, where m is the amount of slope of the calibration curve (meter).[37] Dynamic linear range of the proposed solid phase extraction method was 0.8- 60 µg L^{-1}. The relative standard deviation (RSD) for this method was calculated to be 1.7 with recovery more than 98.3 %. The break through volume was investigated by adding 10 mg of magnetic cadmium IIP into 100, 200, 500, 750 and 1000 mL of a solution containing 0.1 mg Cd (II) ions. The break through volume was calculated to be more than 750 so the enrichment factor is more than 184. Determination of cadmium ions using the developed magnetic SPE was compared to some of the different separation and preconcentration procedures.[34-37] This method is to provide a cleaner extract that is free of matrix interferences with high selectivity and preconcentration factor. Therefore, SPE was modified to enhance selectivity and sensitivity.

The results in Tables 3 indicate that this method possesses good sensitivity, low LOD and high enrichment factor, which is probably because of the large surface area and extraction efficiency.

3.6. Validation of the method

In order to investigate the accuracy of the proposed method, this technique was applied to several reference materials containing certified cadmium amounts. As the results in Table 4 show, there is a good agreement between the certified amounts and this method results. Therefore, this sorbent could be used as a promising solid-phase for extraction and determination of cadmium ions with high accurate results.

3.7. Real samples analysis

The proposed method was applied for determination of trace levels of cadmium ions in used and un-used oil samples. In this regard, after sample preparation by EIEB procedure, the sample solution, which is the acidic aqueous phase containing the extracted metals, was adjusted to pH = 7. Afterward, the amount of cadmium ions was determined in eluent by FAAS after preconcentration by extraction procedure using the magnetic IIP. As the results in Table 5 show, this method is considered to be a reliable and fast method for Cd(II) determination in oil samples. This table shows the results of cadmium ions determination using FAAS, before applying the preconcentration step (direct injection), and after preconcentration using proposed method. The spiking process was also performed in two ways: after extraction induct by EIEB (in acidic solution) and before extraction induct by EIEB (in oil sample).

The results in Table 5 demonstrate that the method has a high recovery for ultra-trace amount of cadmium in diesel oil samples with such a complex matrixes.

The recovery is defined as following equation:

$$\%R = \frac{C_{found} - C_{real}}{C_{aadded}} \times 100 \qquad \textbf{Eq.1}$$

Where C_{found}, $C_{real,}$ and C_{added} are the concentrations of analyte after addition of known amount of standard in the real sample, the concentration of analyte in real sample and the concentration of known amount of standard which was spiked to the real sample, respectively.

3.8. Reusability

The stability of this magnetic IIP was investigated by successive sorption and elution cycles of 100 mL sample solutions containing cadmium ions at the optimum conditions. Afterward, the retained metal ions were eluted by 4 mL of 0.01 mol L^{-1} of $HClO_4$ solution. The results show that the sorbent is stable up to fourteen adsorption-desorption cycles.

4. Conclusion

In this work, a novel ion imprinted polymer grafted on magnetic NPs was synthesized in order to enrich trace levels of cadmium ions in aqueous samples. High surface area, ease of separation due to being magnetic, selectivity and accuracy of the IIP has made it a suitable and reliable sorbent for this purpose. These novel magnetic polymer particles were also used for accurate and selective preconcentration and determination of cadmium ions in diesel oil samples after EIEB and prior to FAAS. The results confirmed that this sorbent could be used successfully for selective extraction of cadmium ions from variety of real sample including oil and aqueous samples.

References:

[1] P. Françoise, S.E. Kreps, M. Bachelet, P. Hainaut, P. Bakonyi, B.S. Polla, Rev. Environ. Health., 2000, **15**, 273.

[2] B. Varga, B. Zsolnai, K. Paksy, M. Náray, G. Ungváry, Reprod. Toxicol., 1993, **7**, 225.

[3] L. Järup, A. Akesson, *Toxicol. Appl. Pharm.*, 2009, **238**, 201.

[4] W.H.O. Staff, Guidelines for drinking-water quality: Surveillance and control of community supplies, second ed., 1997.

[5] R.J. Cassella, D.M. Brum, C.F. Lima, L.F.S. Caldas, C.E.R. De Paula, *Anal. Chim. Acta*, 2011, **690**, 79.

[6] E.M. Becker, M.B. Dessuy, W. Boschetti, M.G.R. Vale, S.L. Ferreira, B. Welz, *Spectrochim. Acta Part B.*, 2012, **71**, 102.

[7] R. Porra, W. Thompson, P. Kriedemann, *Biochim. Biophys. Acta*, 1989, **975**, 384.

[8] B. Bernas, *Anal. Chem.*, 1968, **40**, 1682.

[9] M. Zougagh, A. Torres, J. Cano Pavón, *Talanta*, 2002, **56**, 753.

[10] M. Melo, S. Ferreira, R. Santelli, *Microchem. J.*, 2000, **65**, 59.

[11] B. F. Senkal, I. Muharrem, Y. Erdem, Y. Mehmet, *Talanta*, 2007, **72**, 962.

[12] J Manzoori, G. Karim-Nezhad, *Anal. Chim. Acta*, 2004, **521**, 173.

[13] T. Oymak, S. Tokalıoğlu, V. Yılmaz, S. Kartal, D. Aydın, *Food Chem.*, **113**, 2009, 1314.

[14] D. Lambropoulou, T. Albanis, J. Biochem. Biophys. Meth., 2007, **70**, 195.

[15] A. Richard, T. Wayne, Anal. Chem., 1999, **71**, 652.

[16] M. Tuzen, K. Parlar, M. Soylak, J. Hazard. Mater., 2005, **121**, 79.

[17] M. Hennion, J. Chromatogr. A, 1999, **856**, 3.

[18] M. Lehotay, J. Stajnbaher, F. Schenck, J. AOAC. Int., 2003, **86**, 412.

[19] M. Soylak, L. Elçi, M. Doğan, Anal. Lett., 2000, **33**, 513.

[20] T. Saitoh, S. Suzuki, M. Hiraide, J. Chromatogr. A, 2005, **1097**, 179.

[21] G. Fang, J. Tan, X. Yan, Anal. Chem., 2005, **77**, 1734.

[22] K. Lee, Y. Muraok, M. Oshim, S. Motomizu, Anal. Sci., 2004, **20**, 183.

[23] I. Narin, M. Tuzen, M. Soylak, Talanta, 2004, **63**, 411.

[24] F. Turiel, A. Martín-Esteban, J. Chromatogr. A, 2007, **1152**, 32.

[25] F. Qiao, H. Sun, H. Yan, K. Row, Chromatographia, 2006, **64**, 625.

[26] M. Shamsipur, H.R. Rajabi, Microchim. Acta, 2013, **180**, 243.

[27] M. Shamsipur, H.R. Rajabi, M.H. Beyzavi, H. Sharghi, Microchim. Acta, 2013, **180**, 791.

[28] H.R. Rajabi, M. Shamsipur, S.M. Pourmortazavi, Mater. Sci. Eng. C, 2013, 33, 3374.

[29] H. Ebrahimzadeh , M. Behbahani, Y. Yamini, L. Adlnasab, A. A. Asgharinezhad, Reactive & Functional Polymers, 2013, **73**, 23–29

[30] T. Rao, R. Kala, S. Daniel, Anal. Chim. Acta, 2006, **578**, 105.

[31] L. Yan, L. Zhanchao, W. Yun, D. Jiangdong, G. Jie, X. Jimin, Y. Yongsheng, Microchim. Acta, 2011, **172**, 309.

[32] T. Yang, C. Shen, Z. Li, H. Zhang, C. Xiao, J. Phys. Chem. B, 2005, **109**, 23233.

[33] J. Liu, Z. Zhao, G. Jiang, Environ. Sci. Technol., 2008, **42**, 6949.

[34] X. Liu, Z. Ma, J. Xing, H. Liu, J. Magn. Magn. Mater., 2004, **270**, 1.

[35] O. Sadeghi, M.M. Amini , M. Feiz Bakhsh Bazargani, A. Mehrani, A. Aghabali, M. Adineh, V. Amani, Kh. Mehrani, J. Inorg. Organomet. Polym., 2012, **22**, 530.

[36] R. Cassella, D. Brum, C. Lima, L. Caldas, C. Paula, Anal. Chim. Acta, 2011, **690**, 79.

[37] H. Ebrahimzadeh, N. Tavassoli, O. Sadeghi, M.M. Amini , M. Jamali, Microchim. Acta, 2011, **172**, 479.

[38] Z. Fang, T. Guo , B. Welz, Talanta, 1991, **38**, 613.

[39] M. Esra, T. Mustafa, S. Mustafa, Anal. Chim. Acta, 2006, **578**, 213.

[40] L. Edson, D. Paulo, J. Hazard. Mater., 2009, **161**, 142.

[41] L.Edson, D.Paulo, F.Maria, J. Hazard. Mater., 2009, **171**, 1133.

[42] M. Behbahani, M. Barati, M. Kalate Bojdi, A.R. Pourali, A. Bagheri, N. Akbari Ghareh Tapeh, Microchim. Acta, 2013, **180**, 1117.

[43] M. Gawin, J. Konefał, B. Trzewik, S. Walas, A. Tobiasz, H. Mrowiec, E. Witek, Talanta, 2010, **80**, 1305.

Figure legends:

Figure 1. A schematic diagram for synthesis of cadmium ion imprinted polymer**.**

Figure 2: XRD pattern of synthesized cadmium ion imprinted polymer.

Figure 3. SEM micrograph of synthesized cadmium ion imprinted polymer**.**

Figure 4. Thermal analysis of synthesized cadmium ion imprinted polymer

Figure 5. Effect of pH on cadmium recovery**.** (sample volume: 20 mL, sample concentration: 5 mg L^{-1} of cadmium ions, eluent: 0.01mol L^{-1} $HClO_4$, volume of eluent: 4 mL, time of adsorption: 4 min, time of desorption: 50 min)

Figure 6. Effect of adsorption time on cadmium recovery. (sample volume: 20 mL, sample concentration: 5 mg L^{-1} of cadmium ions, eluent: 0.01mol L^{-1} $HClO_4$, volume of eluent: 4 mL, time of desorption: 50 min, pH:7)

Figure 7. Effect of desorption time on cadmium recovery. (sample volume: 20 mL, sample concentration: 5 mg L^{-1} of cadmium ions, eluent: 0.01mol L^{-1} $HClO_4$, volume of eluent: 4 mL, time of adsorption: 4 min, pH:7)

Table 1. Effect of type, concentration and volume of eluent on recovery of cadmium ions

Eluent	**Volume (mL)**	**Concentration (mol L^{-1})**	**% Recovery**
HCl	10	0.001	67.1
HNO_3	10	0.001	48.9
H_2SO_4	10	0.001	37.5
$HClO_4$	10	0.001	73.6
$HClO_4$	10	0.01	99.4
$HClO_4$	8	0.01	98.7
$HClO_4$	6	0.01	99.2
$HClO_4$	4	0.01	98.8
$HClO_4$	2	0.01	93.1

Table 2. The tolerance limit of diverse ions in the determination of Cadmium

Interfering ions	Tolerable Concentration Ratio X/Cd	Recovery %
Na$^+$	2000	98.3
K+	2000	99.2
Ca^{2+}	2000	99.8
Mg^{+2}	2000	98.6
Zn^{2+}	1000	97.1
Ni^{+2}	1000	97.5
Cu^{+2}	1000	98.3
Co^{+2}	500	96.8
Fe^{+2}	500	98.5
Mn^{+2}	500	97.9
Pb^{+2}	200	96.7

Table 3. Comparison of the separation and preconcentration procedures for cadmium determination

procedure	[a]PF	RSD	DL	Ref.
FAAS-FI	25	13.0%	0.30 μg L^{-1}	[38]
SPE-FAAS	50	5.0%	0.43 μg L^{-1}	[39]
FI-CPE-AAS	20	3.2%	0.75 μg L^{-1}	[40]
CPE-ICP	---	2.6%	1.00 μg L^{-1}	[41]
Nanosized Cd(II)-imprinted polymer-FAAS	300	4.2 %	0.2 μg L^{-1}	[42]
Cd (II)-FI-FAAS	117	2.9 %	0.11 μg L^{-1}	[43]
IIP-FAAS	184	1.7%	0.09 μg L^{-1}	This work

[a] Preconcentration factor

Table 4. Recovery of determination of lead in certified reference materials.

Sample	Uint	Ion	Concentration		Recovery (%)	Relative error (%)
			Certified	Found		
NIST 1571 (Orchard Leaves)	mg kg^{-1}	Cd(II)	0.10	0.104	104.0	3.8
NIST 1572 (Citrus Leaves)	mg kg^{-1}	Cd(II)	0.03	0.029	96.6	3.2

Table 5. The results of determination of cadmium in real samples

sample	Added (μg L^{-1})	Found (μg L^{-1})	Recovery%
Used oil (direct spike to oil) ([b] direct to FAAS)	0 10	3.61 10.46	- 68.5
Used oil (direct spike to oil) ([a]Preconcentration then FAAS)	0 10	3.21 12.31	- 90.9
Unused oil (direct spike to oil) ([b] direct to FAAS)	0 10	4.27 11.54	- 72.7
Unused oil (direct spike to oil) ([a]Preconcentration then FAAS)	0 10	5.01 13.94	- 91.3
Liquid phase of used oil (spike to aqueous phase) ([a]Preconcentration then FAAS)	0 10	3.012 12.71	- 97
Liquid phase of unused oil (spike to aqueous phase) ([a]Preconcentration then FAAS)	0 10	5.01 14.6	- 95.9

[a] Preconcentration with magnetic polymeric nanoparticles

[b] EIEB method

Figure 1

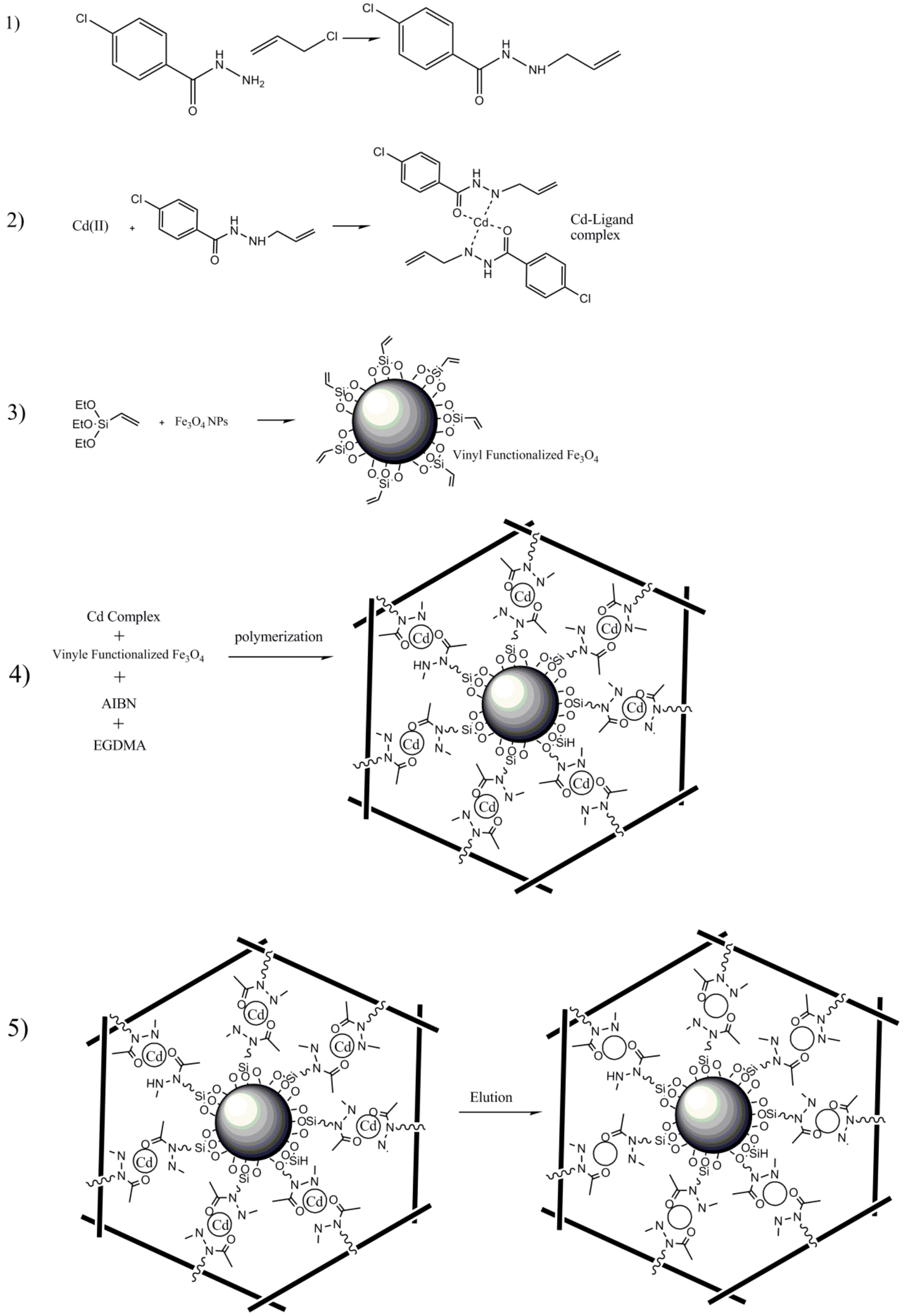

1)
Cl
H
N
NH$_2$
O
Cl
NH
2)
Cd(II)
+
Cd
Cd-Ligand
complex
3)
EtO
EtO-Si
EtO
+
Fe$_3$O$_4$ NPs
Si
O
Vinyl Functionalized Fe$_3$O$_4$
4)
Cd Complex
+
Vinyle Functionalized Fe$_3$O$_4$
+
AIBN
+
EGDMA
polymerization
HN
SiH
5)
Elution

Figure 2:

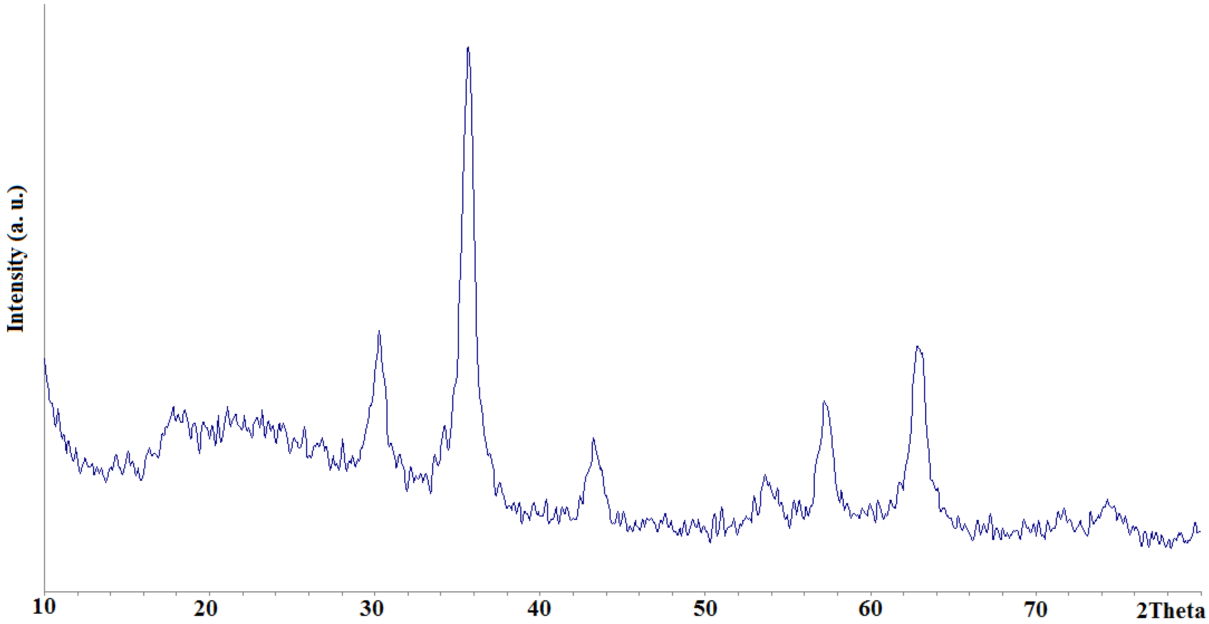


Figure 3.

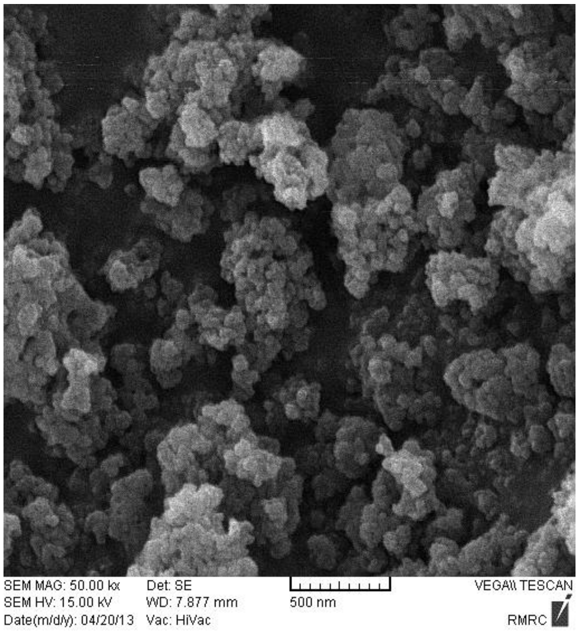

SEM MAG: 50.00 kx
Det: SE
500 nm
VEGA\\ TESCAN
SEM HV: 15.00 kV
WD: 7.877 mm
Date(m/d/y): 04/20/13
Vac: HiVac
RMRC

Figure 4.

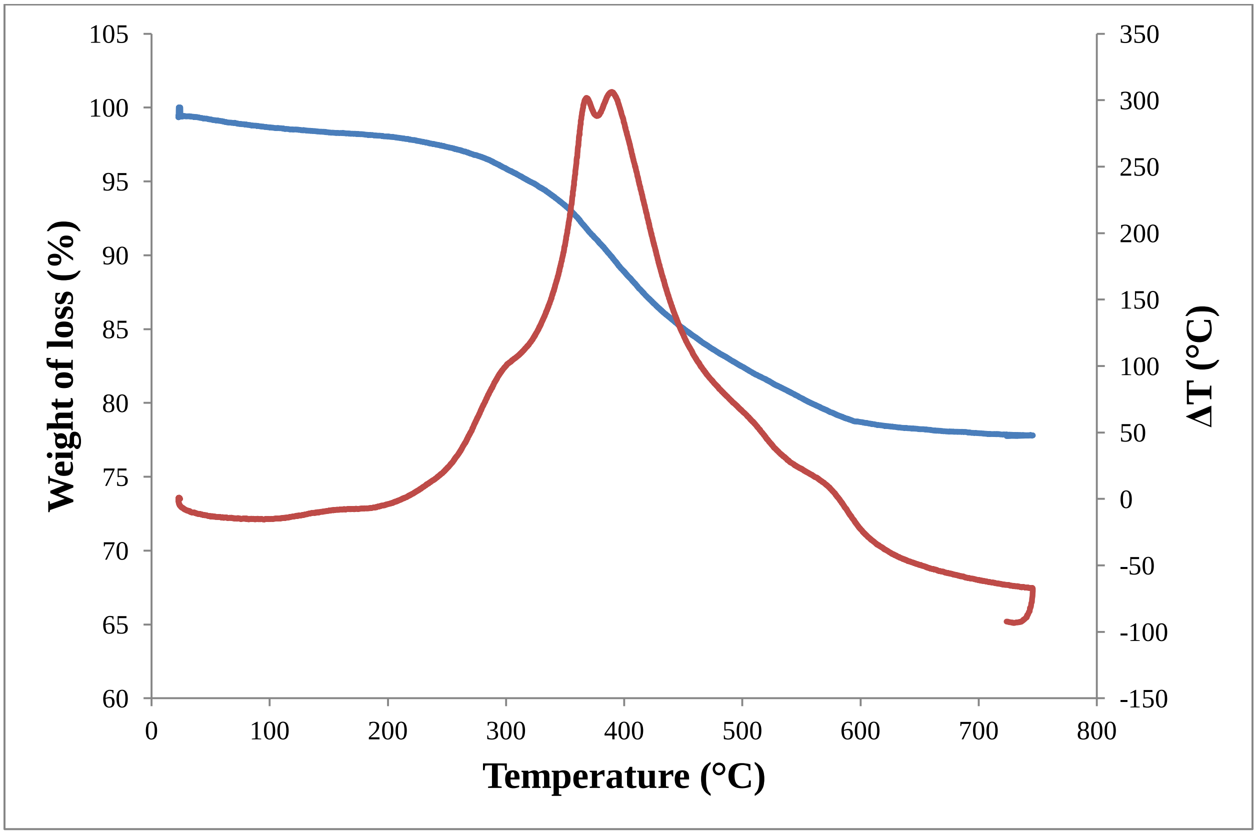

105
100
95
90
85
80
75
70
65
60
Weight of loss (%)
350
300
250
200
150
100
50
0
-50
-100
-150
ΔT (°C)
0
100
200
300
400
500
600
700
800
Temperature (°C)

Figure 5.

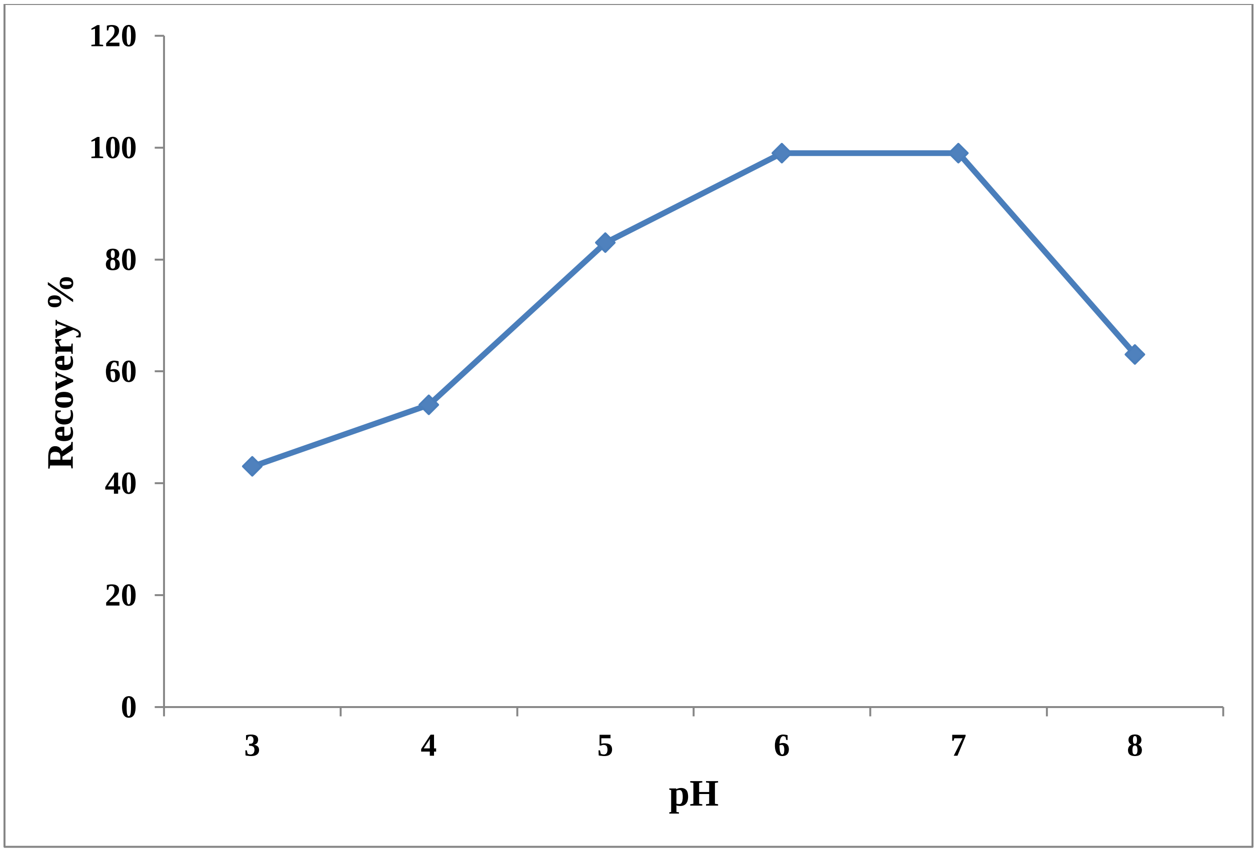
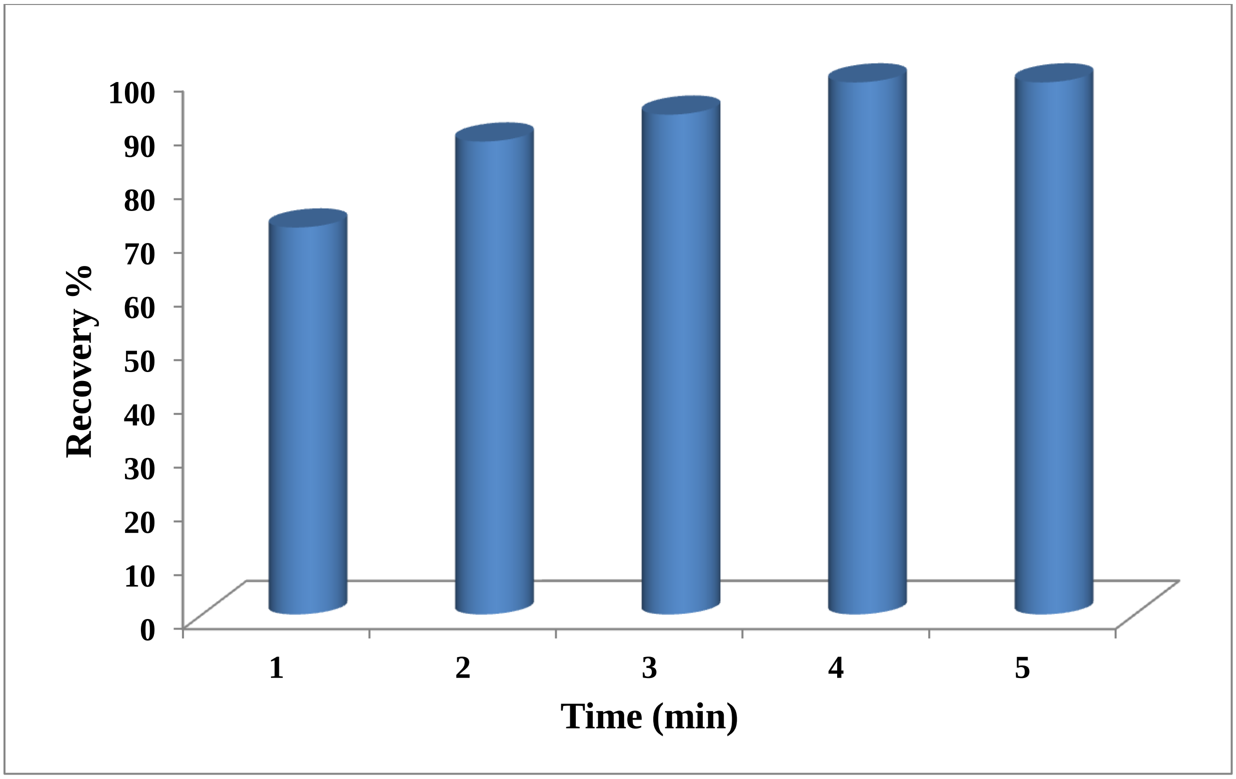
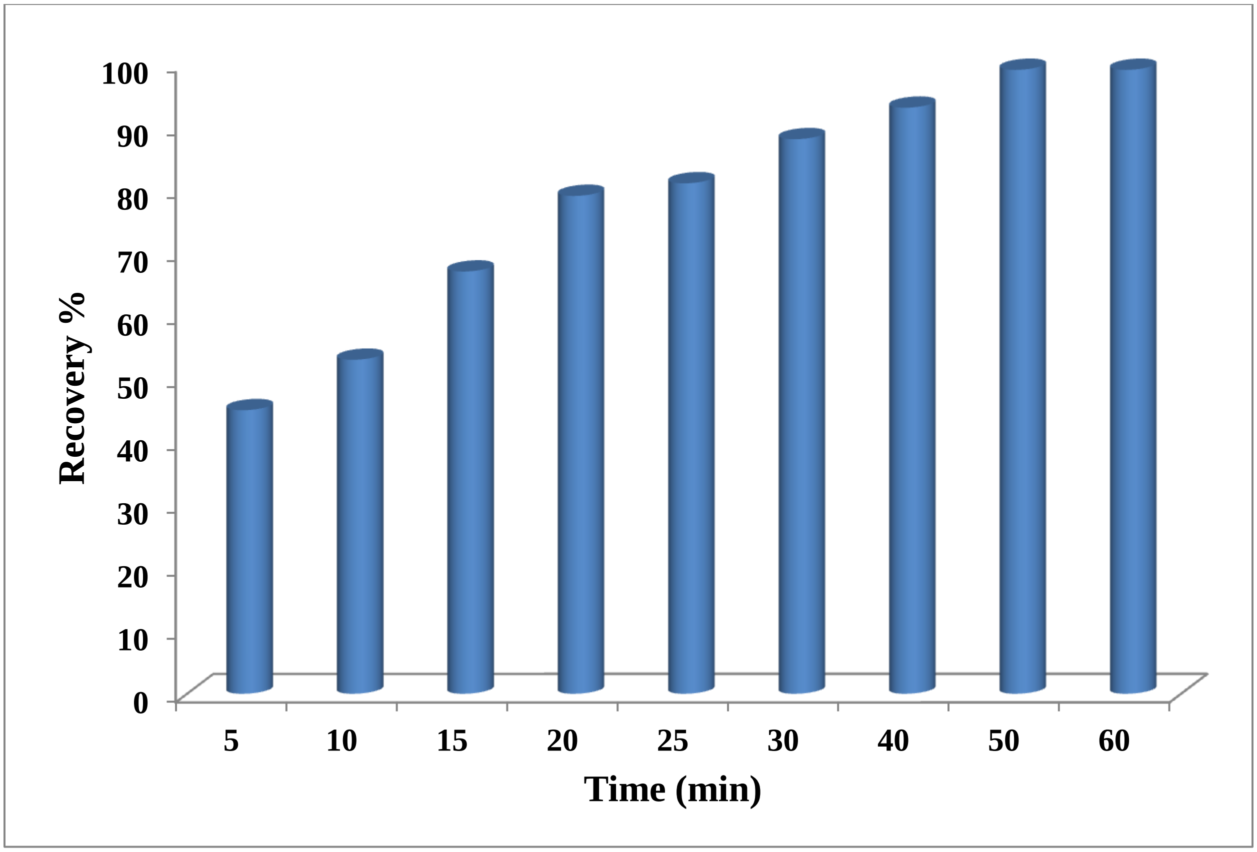


Figure 6.



564 **Figure 7.**



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