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Development of a selective sorbent based on a magnetic ion imprinted polymer for the preconcentration and FAAS determination of urinary cadmium†

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In this study, an ion imprinted polymer (IIP), based on coating of a polymer on a Fe₃O₄ nanoparticle (NP) core, is used as a magnetic sorbent for the preconcentration and determination of the Cd(II) ion level in human urine samples. The synthesized polymer was characterized by IR spectroscopy, scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and thermal analysis (TG/DTA). The optimum conditions, such as pH of the sample, eluent volume, concentration and duration of sorption and elution, were investigated. In addition, the effect of some potentially interfering cations on the sorption of Cd(II) was confirmed. In all samples, Cd(II) was determined using a flame atomic absorption spectrophotometer. Under optimal conditions, the limit of detection (LOD) of cadmium was 0.6 µg L⁻¹. The optimized method has been validated using day-to-day and within-day reproducible experiments and achieved appropriate accuracy and precision. The accuracy of the method was confirmed by analyzing a certified reference material (Seronorm LOT NO2525) and spiked real samples. Ultimately, this method was applied successfully for the preconcentration and determination of Cd(II) ions in urine samples obtained from exposed individuals.

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1. Introduction

One of the major aims of analytical toxicology, whether in the workplace or environment, is the determination of chemical substances in environmental or biological samples. Therefore, international or national societies like ACGIH, OSHA, NIOSH and ISO annually introduce and publish new TLVs (Threshold Limit Values) or PELs (Permissible Exposure Limits).^{1,2} Among various harmful materials, occupational toxicologists pay special attention to determine heavy metals. There is a global concern due to rapid industrial development and release of harmful materials to the environment. Today, most industries use heavy metals directly or indirectly, so that, large numbers of

people are exposed to such materials, particularly heavy metals *via* water, food, air, workplace, and even smoking. Cadmium is one of these heavy metals which is mostly used in plating, battery, welding, semi-conductive and alloy industries.^{2,3} Also, cadmium is a nonessential material element for a human body.^{4,5} On the other hand, according to the IARC ranking, cadmium has sufficient evidence of being a human carcinogen and ranked as Group 1.⁶ Annually, 30 000 tons of cadmium are released into the environment because of natural or human activities. Nevertheless, about 4000 to 13 000 tons of releasing cadmium is because of human activities which are mainly caused by fossil fuel combustion [<https://www.osha.gov/doc/outreachtraining/htmlfiles/cadmium.html>]. Also, OSHA reports that 70 000 individuals are employed in their environment with potential risk of cadmium exposures.⁷ It is proved that cadmium has a harmful effect on the heart, bones, lungs, and chiefly on the kidney. Cadmium could be accumulated on the liver and kidney. After accumulation, it needs about 20 to 30 years to be removed completely from body tissues *via* urine.⁸

According to these facts, evaluation of cadmium is essential. Because of low concentration and intervention of several factors, various separation and preconcentration methods have been developed to evaluate heavy metals such as cadmium.⁹⁻¹¹ Different separation and preconcentration methods such as

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liquid–liquid extraction,¹² solid-phase microextraction,^{13,14} liquid-phase micro-extraction,¹⁵ solid-phase extraction,^{16–18} cloud point extraction,¹⁹ co-precipitation,²⁰ molecular imprinted polymer phase extraction^{21–25} as well as different instrumental analyses like flame atomic absorption spectrometry (FAAS),²⁶ graphite furnace atomic absorption spectrometry (GFAAS),²⁷ and inductively coupled plasma mass spectrometry (ICP-MS)²⁸ have been used for evaluation of metal ions in the spiked or real samples. Among these methods, solid-phase extraction (SPE) has been popularly used for detecting pollutants because of its simplicity, rapidity, cost-benefit, and minimal reagent consumption.²⁹ Ion imprinting is a process in which co-polymerization has been performed between functional and cross-linking monomers in the presence of a target ion (an imprint ion). In order to enhance the sensitivity and selectivity of the SPE procedure, a new sorbent based on an ion imprinted polymer which had synthetic specific sites with high selectivity and affinity for the metal ions was developed.³⁰

Compared to the conventional imprinted polymers, magnetic imprinted polymers have a large surface area and a short diffusion route and consequently high extraction efficiency. Rapid extraction dynamics have been achieved by using such a sorbent.^{31–33}

Fe₃O₄ nano-particles are one of these magnetic particles which have attracted global attention due to their unique physical and chemical properties like biocompatibility, high mass transfer rates, good fluid–solid contact and extraordinary magnetic properties.^{34,35} Recently, a procedure in which combining Fe₃O₄ particles with an ion imprinted polymer (Fe₃O₄@IIP) for extracting metal ions from samples with a complex matrix has been developed.^{36–38}

In this study, a magnetic ion imprinted polymer has been synthesized and applied as a new sorbent for the separation and preconcentration of a trace amount of cadmium from urine followed by its determination with FAAS.

2. Experimental

2.1. Instruments and apparatus

An AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer equipped with an air–acetylene flame and a deuterium lamp background correction was used for the determination of cadmium ions (Kyoto, Japan). A conventional hollow cathode lamp with a wavelength of 228.8 nm was used as the radiation source (Kyoto, Japan). All pH measurements were carried out with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland). Fourier transform infrared spectra (4000–400 cm⁻¹) were recorded on a Bruker IFS-66 FT-IR Spectrophotometer (Massachusetts, USA). The morphology and size of the magnetic IIP were observed with a Philips scanning electron microscope (XL-30, Almelo, The Netherlands). The thermal gravimetric and differential thermal analysis (TG-DTA) was carried out on a BAHRTHERMO analysis GmbH (Hüllhorst, Germany) under an air atmosphere at the heating rate of 10 °C min⁻¹. The X-ray diffraction (XRD) patterns were achieved on a Philips-PW12C diffractometer (Amsterdam, The Netherlands) with Cu K α radiation.

2.2. Chemicals and reagents

All reagents were of analytical grade and were purchased from Merck (Darmstadt, Germany). A 1000 mg L⁻¹ standard solution of Cd(II), as well as HCl, HNO₃, N(CH₂CH₃)₃, toluene, acetonitrile, 2-aminobenzothiazole, FeCl₃, FeSO₄, NaOH, NH₄OH (32% solution), azobisisobutyronitrile (AIBN), ethylene glycol dimethacrylate (EGDMA), 3-chloro-1-propane and trimethoxy vinyl silane were purchased from Merck. The working solutions of Cd(II) were obtained by diluting the standard solution with deionized water, and diluted HCl and NaOH were used to adjust pH values to the various ranges. All the required solutions were prepared using deionized water provided by a Milli-Q (Millipore, Bedford, MA, USA) purification system.

2.3. Procedures

2.3.1. Preparation of Fe₃O₄ nanoparticles. Fe₃O₄ NPs were synthesized according to a previously reported procedure.³³ Briefly, 10.4 g of FeCl₃·6H₂O and 4.0 g of FeCl₂·4H₂O were dissolved in 100 mL of deionized water, degassed with nitrogen gas for 15 min and heated to 80 °C. Then, 15 mL of NH₄OH (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 NPs was confirmed by IR spectroscopy and X-ray powder diffraction.

2.3.2. Preparation of vinyl functionalized Fe₃O₄. Vinyl functionalization of Fe₃O₄ NPs was performed by the reaction of silane agents with Fe₃O₄ NPs according to a recent report.³⁹ To prepare vinyl functionalized Fe₃O₄ NPs, 1.0 g of prepared Fe₃O₄ NPs was suspended in 50 mL of toluene, following this, 1.0 g of 3-vinyltriethoxysilane was added to the solution and the mixture was stirred for 24 hours. The solid phase was separated from the solvent by a magnet and washed three times with 50 mL of acetone in order to remove any impurities, and then dried at room temperature.

2.3.3. Preparation of a vinylated ligand. 2-Aminobenzothiazole has S and N atoms which show a high tendency to coordinate with cadmium ions, selectively. Furthermore, in the following references, thiazole ligands are used as a complexing agent for cadmium/heavy metal determination.⁴⁰ In this step, a vinylated ligand was prepared by the reaction of 2-aminobenzothiazole as a ligand (1 mmol) and of 3-chloro-1-propane (1 mmol) in 50 mL solution of triethylamine and methanol (1 : 4 v/v) at room temperature. After 4 hours, the solvent was removed under the reduced pressure.

2.3.4. Preparation of the Fe₃O₄@IIP nanosorbent. For a synthesis of the Cd(II) nano IIP, by a typical polymerization reaction, a two-necked glass reactor was equipped with a condenser, a magnetic stirrer and a gas inlet to maintain a nitrogen atmosphere. One mmol of the complex and 1.0 g of vinyl functionalized Fe₃O₄ were dispersed in 100 mL of methanol, then, the mixture temperature was raised to 70 °C and afterwards 0.08 g of AIBN and 1.1 mL of EGDMA were added. After 48 hours, the nano IIP was separated by a magnet, and the template (cadmium ions) was removed by a solution containing 1 mol L⁻¹ HCl.

In order to confirm the removal of Cd(II) ions, a small amount of the magnetic polymer was treated with piranha solution, then Cd(II) ions were determined by FAAS. Piranha solution, containing concentrated H₂SO₄ and 30% solution of H₂O₂ (3 : 1 v/v), dissolves the polymer network as well as Fe₃O₄ NPs and releases metallic ions in solution, which can be determined by FAAS.³⁹ It is important to remark that this process was performed just on 20 mg of the polymer as a trial experiment to confirm that an efficient removal of the Cd(II) ion template by acidic elution was accomplished. Therefore, the results showed that eluting with HCl solution is sufficient for Cd(II) removal. The formation of this IIP was confirmed by IR spectroscopy, TG/DTA analysis, XRD and SEM. A schematic diagram of the magnetic IIP is shown in Fig. 1.

2.4. Extraction procedure

The extraction procedure consists of two steps: in the sorption step, the pH of sample solution was adjusted at 7.0, then, 20 mg of the magnetic IIP was suspended in the aqueous solution

containing 0.5 mg L⁻¹ of Cd(II) and stirred for 5.0 min. After washing with 5 mL distilled water, in the next step elution of adsorbed Cd(II) ions was performed with 4.0 mL of 2 mol L⁻¹ HCl solution for five minutes. The concentration of cadmium ions in the eluent was evaluated by FAAS.

2.5. Real samples

The urine samples were obtained from workers employed in one of the automobile industries (Tehran, Iran). The samples were collected in sterile sample containers and were kept in the refrigerator (4 °C). It is worth mentioning that all experiments were performed in compliance with the relevant laws and institutional guidelines, and also the institutional committee has approved the experiments. Digestion of urine certified reference material (Seronorm LOT NO 2525) powder was performed in a reaction vessel containing 2 mL of HNO₃ (1% v/v) and 2 mL of H₂O₂ (30% v/v) and was placed in an ultrasonic bath for 30 min. Then the solution was diluted to 5 mL using deionized water.⁴¹ To determine the Cd(II) content in urine

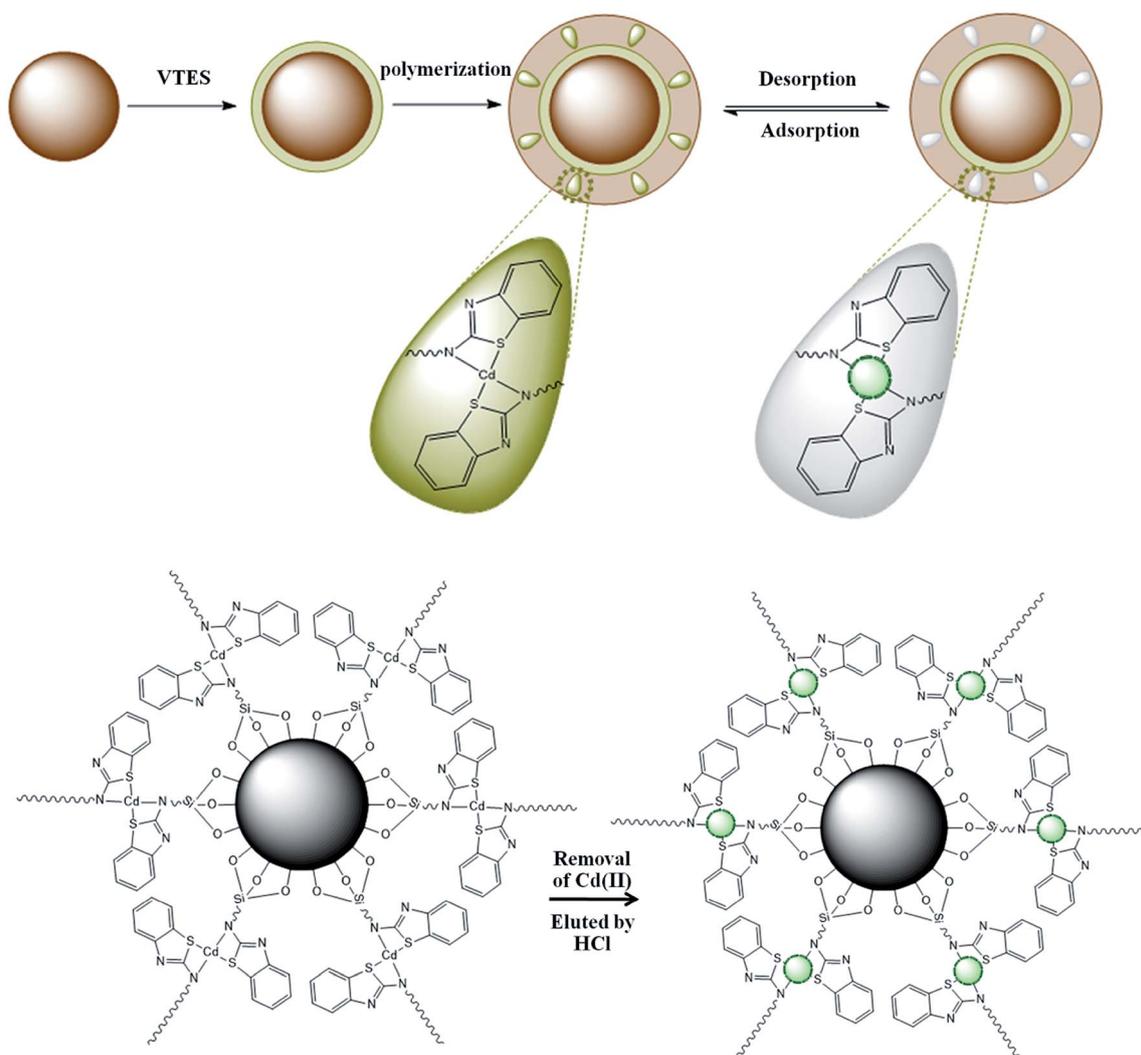


Fig. 1 A schematic diagram for the synthesis process of the magnetic ion imprinted polymer of cadmium.

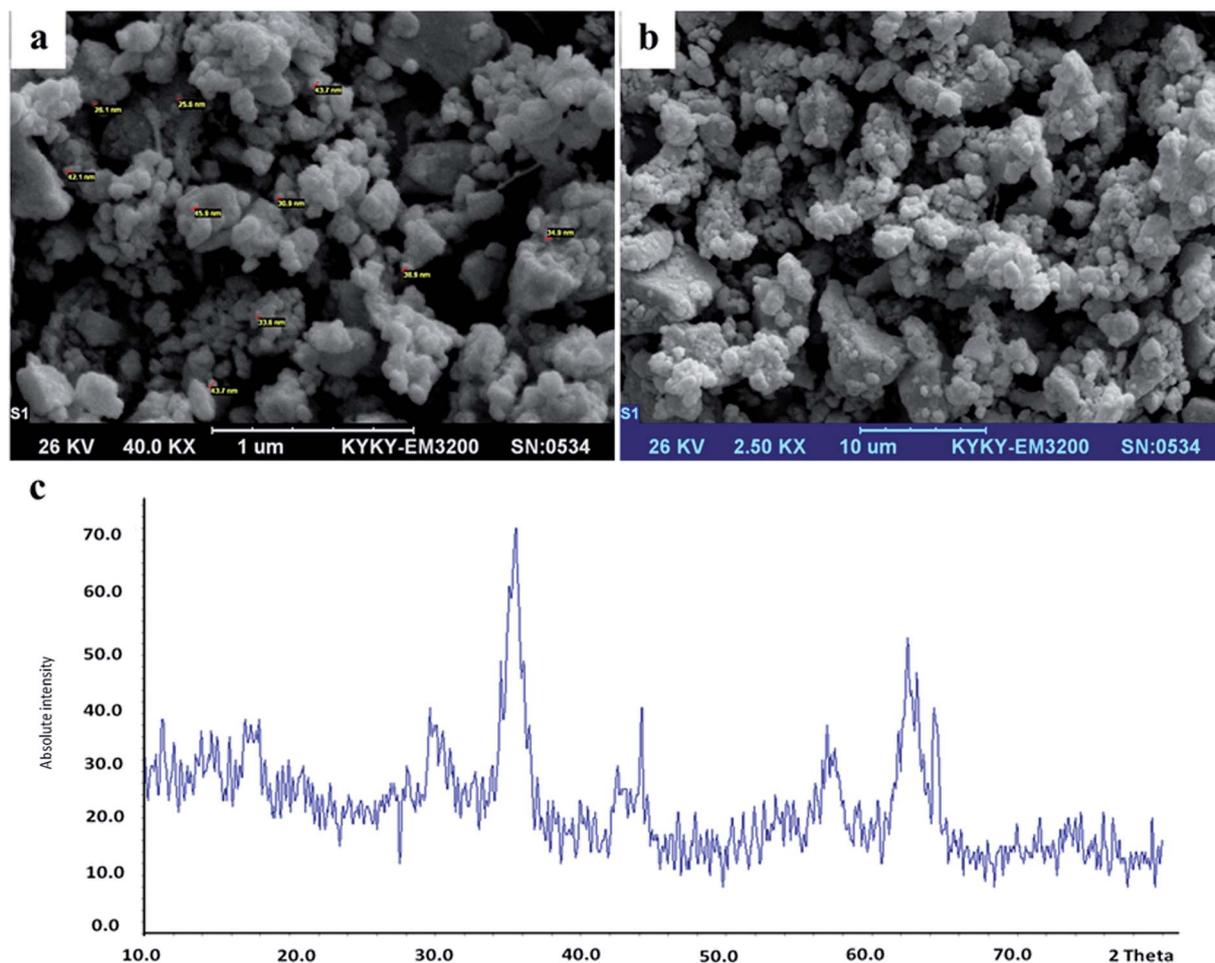


Fig. 2 1 μm (a) and 10 μm (b) scaled SEM micrographs of the synthesized magnetic IIP; (c) XRD pattern of the magnetic IIP.

samples, 20 mg of the prepared sorbent was weighed and suspended in 20 mL of urine. Then, by using a standard addition method (SAM), Cd(II) concentrations were determined in each sample under the optimized condition by FAAS.

3. Results and discussion

3.1. Sorbent characterization

Formation of Fe_3O_4 NPs has been assessed by IR spectroscopy, SEM and XRD analysis. Modification of the Fe_3O_4 NP surface with vinyl groups was carried out through the direct method for the functionalization of Fe_3O_4 with triethoxysilane agents reported before.⁸ The reaction of vinyl functionalized Fe_3O_4 with a vinylated ligand complex as another monomer in the presence of Cd(II) as a template, AIBN as an initiator and EGDMA as a cross-linker causes the formation of this magnetic IIP (Fig. 1).

The synthesized imprinted polymer was characterized by IR spectroscopy, SEM, and TG/DTA analysis. The FT-IR spectra of the IIP showed the following bands: C=S (1145 to 1149 cm^{-1}), C=N (1629 to 1632 cm^{-1}) and N-H (3415 to 3437 cm^{-1}) as shown in Fig. 1S.[†] The thermal stability of this nano IIP was evaluated by TG/DTA analysis (Fig. 2S[†]). The results showed that Fe_3O_4 @Cd-IIP may be stable at high temperatures, as it was

stable up to $300\text{ }^\circ\text{C}$. Nevertheless, according to the loss of 20% of the composite weight, it can be concluded that the composite was burned causing a 20% loss of its weight. This reduction was belonged to the polymer and the residue was contributed to Fe_3O_4 . In addition, the size and morphology assessment of the

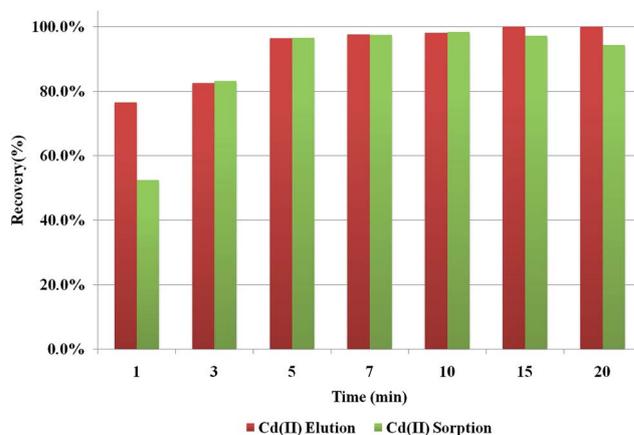


Fig. 3 Effect of sorption and elution times on the recovery of Cd(II), conditions: sample pH, 7.0; eluent volume, 4.0 mL (2 mol L^{-1} HCl).

synthesized sorbent were confirmed by SEM (Fig. 2a and b). By investigating these micrographs, it became apparent that the sorbent consists of spherical NPs with approximately 40 nm diameter. It is worth mentioning that, since the magnetic NPs are coated with the polymer, they will not be destroyed in acidic solutions.⁹

According to the XRD pattern, the Fe₃O₄ structure remained unchanged after polymerization; it means that Fe₃O₄ did not decompose or convert to Fe₂O₃. Also, according to Fig. 2c, and the Scherrer equation, the broad peaks in the XRD pattern show that Fe₃O₄ is in the nanosized scale. The average crystallite size of the magnetic IIP was estimated from the XRD pattern using the Scherrer formula:

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

where D is the average crystallite size, λ is the X-ray wavelength, 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 the magnetic IIP was computed from the XRD pattern and found to be about 28 nm. The XRD pattern of Fe₃O₄@IIP showed that the length of peaks reduced compared to the Fe₃O₄ XRD pattern. It can be concluded that Fe₃O₄ nanoparticles have been coated with polymer compounds.

3.2. Optimization of the preconcentration method

3.2.1. Effect of sample pH. The pH factor has the ability to change the coordination sites of the ligand, so, it will be one of the most controlling parameters for the sorption of Cd(II) on the synthesized polymer. In order to explore the effect of this parameter, the pH values were adjusted in the range of 3.5–8.0. After stirring for 5.0 min, the adsorbed Cd(II) ions were eluted with 4.0 mL of 2 mol L⁻¹ HCl, subsequently, the amount of Cd(II) ions in the eluent was determined by FAAS (Fig. 3S†). The optimized sample pH for the adsorption of Cd(II) onto the magnetic IIP was 7.0. At low pH values, there is an excessive protonation of the lone pair of electrons on nitrogen and sulfur, resulting in a decrease in the Cd(II) ion sorption. Moreover, in the alkaline pHs, Cd(II) precipitates as Cd(OH)₂ causing a decrease in sorption efficiency.

3.2.2. Effect of eluent type, volume and its concentration. In order to elute Cd(II) from the IIP, HCl was chosen among H₂SO₄, HNO₃ and HCl. The inspection of the effect of eluent volume on the recovery of Cd(II) showed that 4.0 mL of 2 mol L⁻¹ HCl was the optimum volume for elution of Cd(II) ions. Interestingly, at larger volumes, the recoveries were not significantly raised by increasing the eluent volume. Therefore, to obtain higher preconcentration factors, 4.0 mL of 2 mol L⁻¹ HCl was the optimum eluent for the extraction of cadmium.

3.2.3. Optimization of sorption and elution time. The effect of time is one of the important factors in the analytical process while inadequate time reduces the procedure efficiency extra time lowers the throughput. In order to investigate the effect of time, 25 mL of solutions containing 0.5 mg L⁻¹ of Cd(II) was adjusted to pH = 7.0 and 20 mg of the magnetic IIP was suspended in the solutions and stirred for various durations

and at the end of this process, it was washed with 5.0 mL distilled water. Then, the sorbent was separated by placing a magnet and the pre-concentrated analyte was determined by FAAS after eluting with 2 mol L⁻¹ HCl. According to Fig. 3, both optimized sorption and elution times were selected as 5.0 min. This fast extraction and elution duration could be attributed to the high surface area dealing with these IIP NPs. Compared to a column technique, the magnetic method takes shorter sorption and desorption times.^{14,17,18}

3.2.4. Influence of potentially interfering ions. In various matrices even biological ones, there are unknown potentially interfering agents. In order to extract Cd(II), several cations may cause a decrease in recovery. So, the method of extraction must be selective enough to measure an accurate value of Cd(II) even in complex matrices. In order to investigate the selectivity of the sorbent, the effect of some cations was assessed. For this purpose, 0.5 mg L⁻¹ of Cd(II) ion solutions containing, individually the interfering ions, Na⁺, Pb²⁺, Zn²⁺, and Cu²⁺ were analyzed under optimum conditions. Also the X ion concentration was 2000 times of the Cd(II) ions (Table 1S†). The tolerable amount was defined as the maximum concentration that could cause a change of less than 5% in a signal compared to the signal of Cd(II) ions without any interference.⁹ As shown in Table 1S,† none of these ions interfere with the concentrations encountered in biological samples, and the method is selective toward Cd(II) extraction at pH = 7.0. This high selectivity could be attributed to very selective sites, the size and shape of which are fitted to the Cd(II) ions specifically.

It is worth mentioning that, based on the obtained results, the IIP procedure is promising to be more selective. The phase

Table 1 Determination of Cd(II) ions in the certified reference material

Sample	Concentration (µg L ⁻¹)		Relative error (%)
	Certified	Found	
Seronorm LOT NO2525	5.06	5.23	3.4

Table 2 Measurement of Cd(II) in urine samples by using the magnetic IIP

Sample	Age	Smoking habit	Job	Concentration of urine (µg L ⁻¹)
1	32	No	Painting	84.0
2	30	No	Painting	54.0
3	31	No	Painting	29.2
4	32	Yes	Painting	72.3
5	30	Yes	Painting	15.0
6	31	No	Painting	20.0
7	31	No	Welding	147
8	27	No	Welding	21.3
9	33	Yes	Welding	142
10	42	No	Welding	52.0
11	26	No	Welding	28.0

Table 3 Comparative LOD of various methods for the determination of Cd(II) in urine samples

Type of samples	Preparation method	Analytical method	LOD ($\mu\text{g L}^{-1}$)	Ref.
Urine	Modification of a matrix with diammonium hydrogen phosphate/nitric acid	GFAAS	0.09	42
Urine	Digestion with nitric acid	AAS	5.67	42
Urine	Dilution with nitric acid	ETAAS	0.045	42
Biological	$\text{Fe}_3\text{O}_4@\text{SiO}_2$ Cd^{2+}	ETAAS	0.19	17
Urine	$\text{Fe}_3\text{O}_4@\text{IIP}$ Cd^{2+}	FAAS	0.6	This study

can be synthesized in a short time followed by a simple protocol for the extraction stage, making the method to be more convenient compared to the usual silica based SPE technique.

3.2.5. Analytical figures of merit. In order to prove the precision and accuracy of the present technique, the reproducibility of the optimized method was validated for day-to-day and within-day reproducibility using spiked aqueous samples. 25 mL of samples were used at low, medium, and high concentrations of 2, 10, and 50 $\mu\text{g L}^{-1}$, respectively. A linear standard curve was obtained for extracting samples over the range of concentrations everyday for 6 consecutive days ($n = 6$) with the correlation coefficient of 0.997 or greater. From within-day experiments, evaluation, six experiments were performed each day for three consecutive days. The extraction procedure was reliable and reproducible for day-to-day and within-day. The coefficient of variations (CV%) of 0.092, 0.064, and 0.017 were obtained for 2, 10, and 50 $\mu\text{g L}^{-1}$ respectively, for day-to-day and 0.146, 0.058, and 0.014 at the same concentrations, respectively for within-day, showing appropriate accuracy and precision for the optimized method (Table 2S[†]).

It is worth mentioning that cadmium in samples was determined using a standard addition method and a linear curve was plotted ($R^2 > 0.98$).

3.2.6. Method validation. In order to establish the accuracy of the current method, the concentration of Cd(II) ions was compared with the exact concentration of this ion in the certified reference material (Seronom LOT NO2525) and the result was in good agreement with the certified value (Table 1).

3.2.7. Determination of urinary cadmium. The optimized method was applied for the determination of Cd(II) ion concentration in urine samples collected from male workers from one of the Iranian automobile industries whom are exposed to Cd(II) through welding and painting processes. In this regard, after the collection and shipping of the sample to the analytical laboratory, each sample was divided into 3 parts. Then Cd(II) values were determined in each sample under optimized conditions by using a standard addition technique (Table 2).

According to the available research studies, analytical performance of those methods which used a specific instrument like a graphite furnace atomic absorption spectrometer (GFAAS) or an electrothermal atomic absorption spectrometer (ETAAS) is better than FAAS: 0.09, 0.045 and 5.75 $\mu\text{g L}^{-1}$ respectively. Utilization of preconcentration techniques can cause an increase in the performance of the analytical method carried out by FAAS.

This method had not been used for the extraction of metallic ions through urine samples. Furthermore, according to the ATSDR profile of Cd(II), the lowest LOD for the determination of Cd(II) by the FAAS method was 5.67 $\mu\text{g L}^{-1}$,⁴² in which, the obtained LOD of the present study was 0.6 $\mu\text{g L}^{-1}$ (Table 3). The excellent sensitivity of magnetic IIP extraction allows researchers to determine a trace concentration of Cd(II) in urine samples. Also, there is no need to use instruments like a Graphite Furnace Atomic Absorption Spectrometer (GFAAS) or an Electrothermal Atomic Absorption Spectrometer (ETAAS) in similar studies. On the other hand, the measurement of Cd(II) using the $\text{Fe}_3\text{O}_4@\text{IIP}$ needs no pretreatment like acidic digestion, filtration, or centrifugation.

4. Conclusion

A new magnetic ion imprinted polymer (IIP) has been synthesized by coating an IIP on the surface of Fe_3O_4 nanoparticles to achieve the highest surface area for extraction. The selectivity of this ion imprinted polymer has made it to be a suitable and selective sorbent for the extraction and preconcentration of cadmium ions in biological samples. In order to achieve the best performance by least expense optimum parameters, *i.e.* pH = 7.0, sorption and elution times are set to 5.0 min and the eluent volume of 4.0 mL (2 mol L^{-1} HCl) is used. The high selectivity of this magnetic IIP can determine Cd(II) in biological samples without the need for an unintelligible instrument like a GFAAS or an ETAAS, reducing costs and saving time. Other advantages of this method are due to the magnetically assisted separation of the sorbent and high surface area; therefore, satisfactory results can be achieved using a lower quantity of the sorbent. On the other hand, according to day-to-day and within-day reproducibility experiments, this technique has an acceptable degree of reliability for analyzing biological samples.

References

- 1 M. Ghaedi, F. Ahmadi and M. Soylak, *J. Hazard. Mater.*, 2007, **147**, 226–231.
- 2 G. D. Matos and M. A. Z. Arruda, *Spectrosc. Lett.*, 2006, **39**, 755–768.
- 3 M. Soylak, A. U. Karatepe, L. Elçi and M. Doğan, *Turk. J. Chem.*, 2003, **27**(2), 235–242.
- 4 S. E. Manahan, *Environmental Chemistry*, Lewis Publishers, Boca Raton, 6th edn, 1994.

- 5 B. G. Katzung, *Basic and Clinical Pharmacology*, Appleton and Lange, Norwalk, CT, 3rd edn, 1989.
- 6 IARC, *Scand. J. Work, Environ. Health*, 1993, **19**, 360–363.
- 7 OSHA, Office of Regulatory Analysis 1992.
- 8 National Library of Medicine, Hazardous Substances Data Bank (HSDB) 1996.
- 9 O. Sayar, N. Akbarzadeh-Torabi, H. Saravani, K. Mehrani, A. Behbahani and H. R. Moghadam-Zadeh, *J. Ind. Eng. Chem.*, 2013, **20**(5), 2657–2662.
- 10 M. Soyлак, I. Narin and M. Dogan, *Anal. Lett.*, 1997, **30**(15), 2801–2810.
- 11 V. N. Bulut, A. Gundogdu, C. Duran, H. B. Senturk, M. Soyлак, L. Elci and M. Tufekci, *J. Hazard. Mater.*, 2007, **146**(1–2), 155–163.
- 12 I. Komjarova and R. Blust, *Anal. Chim. Acta*, 2006, **576**, 221–228.
- 13 H. R. Heidari, S. J. Shahtaheri, F. Golbabaei, M. Alimohamadi and A. Rahimi-Froushani, *Iran. J. Public Health*, 2009, **38**(1), 89–99.
- 14 F. Ghavidel, S. J. Shahtaheri, M. Torabbeigi and A. Rahimi-Froushani, *Am. J. Chem.*, 2014, **5**(9), 535–546.
- 15 S. Nazari, *Microchim. Acta*, 2008, **90**(2), 107–112.
- 16 A. Baysal, N. Tokman and S. Akman, *Int. J. Environ. Anal. Chem.*, 2008, **88**(3), 141–150.
- 17 G. Giakissikli and A. N. Anthemidis, *Anal. Chim. Acta*, 2013, **789**, 1–16.
- 18 S. J. Shahtaheri, M. Khadem, F. Golbabaei and A. Rahimi-Froushani, *Iran. J. Public Health*, 2007, **36**(2), 73–81.
- 19 X. D. Wen, P. Wu, L. Chen and X. D. Hou, *Anal. Chim. Acta*, 2009, **650**(1), 33–38.
- 20 T. Oymak, S. Tokalioglu, V. Yilmaz, S. Kartal and D. Aydin, *Food Chem.*, 2009, **113**, 1314–1317.
- 21 H. Ebrahimzadeh, M. Kasaeian, A. Khalilzadeh and E. Moazzen, *Anal. Methods*, 2014, **6**, 4617–4624.
- 22 M. Rahiminejad, S. J. Shahtaheri, M. R. Ganjali, A. Rahimi-Froushani, A. R. Koohpaei and F. Golbabaei, *Iran. J. Environ. Health Sci. Eng.*, 2009, **6**(2), 97–106.
- 23 A. R. Koohpaei, S. J. Shahtaheri, M. R. Ganjali, A. Rahimi-Froushani and F. Golbabaei, *J. Hazard. Mater.*, 2009, **170**, 1247–1255.
- 24 M. Rahiminejad, S. J. Shahtaheri, M. R. Ganjali, A. Rahimi-Froushani, A. R. Koohpaei and F. Golbabaei, *J. Anal. Chem.*, 2010, **65**(7), 694–697.
- 25 F. Omidi, M. Behbahani, H. Sadeghi Abandansari and S. J. Shahtaheri, *Iran. J. Public Health*, 2014, **43**(5), 645–657.
- 26 L. Haixia, A. Hongtao and X. Zenghong, *Int. J. Biol. Macromol.*, 2013, **56**, 89–93.
- 27 M. Ueda, N. Teshima, T. Sakai, Y. Joichi and S. Motomizu, *Anal. Sci.*, 2010, **27**, 597–602.
- 28 N. Zhang and H. Bin, *Anal. Chim. Acta*, 2012, **723**, 54–60.
- 29 M. Tuzen, K. O. Saygi and M. Soyлак, *J. Hazard. Mater.*, 2008, **156**, 591–595.
- 30 T. P. Rao, R. Kala and S. Daniel, *Anal. Chim. Acta*, 2006, **578**, 105–116.
- 31 L. G. Chen, X. J. Zhang, L. Sun, Y. Xu, Q. L. Zeng, H. Wang, H. Y. Xu, A. M. Yu, H. Q. Zhang and L. Dung, *J. Agric. Food Chem.*, 2009, **57**, 10073–10080.
- 32 M. Zhang, Z. Zhang, Y. Liu, X. Yang, L. Luo, J. Chen and S. Yao, *Chem. Eng. J.*, 2011, **178**, 443–450.
- 33 Y. H. Deng, D. W. Qi, C. H. Deng, X. M. Zhang and D. Y. Zhao, *J. Am. Chem.*, 2008, **130**, 28–29.
- 34 C. J. Tan and Y. W. Tong, *Anal. Chem.*, 2007, **79**, 299–306.
- 35 S. H. Xuan, Y. X. J. Wang, K. C. F. Leung and K. Y. Shu, *J. Phys. Chem.*, 2008, **112**, 18804–18809.
- 36 A. A. Asgharinezhad, H. Ebrahimzadeh, M. Rezvani, N. Shekari and M. Loni, *Food Addit. Contam.*, 2014, **31**(7), 1196–1204.
- 37 M. Rezvani, A. A. Asgharinezhad, H. Ebrahimzadeh and N. Shekari, *Microchim. Acta*, 2014, **181**, 1887–1895.
- 38 A. A. Asgharinezhad, N. Mollazadeh, H. Ebrahimzadeh, F. Mirbabaei and N. Shekari, *J. Chromatogr. A*, 2014, **1338**, 1–8.
- 39 H. Ebrahimzadeh, E. Moazzen, M. Amini and O. Sadeghi, *Anal. Methods*, 2012, **4**, 3232–3237.
- 40 G. Grigoropoulou, P. Stathi, M. A. Karakassides, M. Louludi and Y. Deligiannakis, *Colloids Surf., A*, 2008, **320**, 25–35.
- 41 G. Daneshvar Tarigh and F. Shemirani, *Talanta*, 2013, **115**, 744–750.
- 42 ATSDR, *Toxicological Profile For Cadmium*, U.S. Department of Health and Human Services Public Health Service, September 2012, Section 7 (Analytical methods, 333–343).