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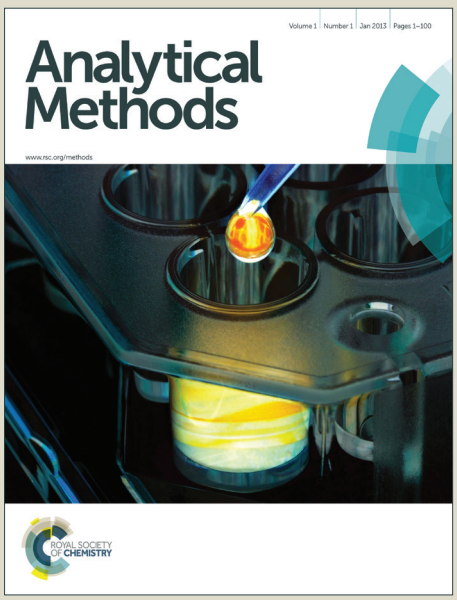

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Development of selective sorbent based on magnetic ion imprinted polymer for preconcentration and FAAS determination of urinary cadmium

Zahra Panjali[1], Ali Akbar Asgharinezhad[2], Homeira Ebrahimzadeh[2], Sara Karami[2], Masood Loni[2], Mehdi Rezvani[2], Rasoul Yarahmadi[3], Seyed Jamaleddin Shahtaheri[*1,4]

[1]*Department of Occupational Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran*
[2] *Department of Applied Chemistry, School of Chemistry, Shahid Beheshti University, Tehran, Iran*
[3]*Department of Occupational Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran*
[4]*Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran*

*Corresponding author E-mail: *shahtaheri@tums.ac.ir* Tel/Fax: +9821 8895 1390 (Seyed Jamaleddin Shahtaheri)

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Abstract

In this study an ion imprinted polymer (IIP), based on coating of polymer on Fe_3O_4 nanoparticles (NPs) core, was used as a magnetic sorbent for preconcentration and determination of Cd(II) ion level in human urine samples. 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 firmed. In all samples, Cd(II) was determined by flame atomic absorption spectrophotometer. Under optimal conditions, the detection limit (LOD) of cadmium was 0.6 μg L^{-1}. The optimized method has been validated using day-to-day and within-day reproducibly 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.

Key words: Cd(II); Magnetic ion imprinted polymer; Selective extraction; Urine samples.

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1. Introduction

One of the major aims of analytical toxicology whether in the workplace or environment is 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 value) or PELs (Permissible Exposure Limits) [1-2]. Among various harmful materials, occupational toxicologists put special attention on determination of heavy metals. There is global concern due to rapid industrial development and releasing harmful materials to the environment. Today, most of industries use heavy metals directly or indirectly, so that, large numbers of people are exposed to such material, particularly heavy metals via water, food, air, workplace, and even smoking. Cadmium is one of these heavy metals mostly is used in plating, battery, welding, semi-conductive and alloys industries [2-3]. Also, cadmium is a nonessential material element for human body [4-5]. On the other hand, according to IARC ranking, cadmium has sufficient evidence of being human carcinogen and ranked as Group 1 [6]. Annually, 30000 tons of cadmium are released into the environment because of natural or human activities. Nevertheless, about 4000 to 13000 tons of releasing cadmium is because of human activities which mainly caused by fossil fuels combustion [https://www.osha.gov/doc/outreachtraining/htmlfiles/cadmium.html]. Also, OSHA reports that 70000 individuals are employed in their environment with potential risk of cadmium exposures [7]. It is proved that, cadmium has a harmful effect on heart, bones, lungs, and chiefly on the kidney. Cadmium could be accumulated on 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

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preconcentration methods such as 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 analysis like flame atomic absorption spectrometry (FAAS) [26], graphite furnace atomic absorption spectrometry (GFAAS) [27], inductively coupled plasma mass spectrometry (ICP-MS) [28] have been used for evaluation of metal ions in the spiked or real samples. From these methods, solid-phase extraction (SPE) has been popularly used for detecting pollutants because of 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 the target ion (the imprint ion). In order to enhance the sensitivity and selectivity of SPE procedure, new sorbent based on 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 large surface area and short diffusion route and consequently high extraction efficiency. Rapid extraction dynamics have been achieved by using such sorbent [31-33].

Fe_3O_4 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 Fe_3O_4 particles with ion imprinted polymer (Fe_3O_4@IIP) for extracting metal ions from samples with complex matrix has been developed [36-38].

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

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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 ion (Kyoto, Japan). Conventional hollow cathode lamp with wavelength 228.8 nm was used as the radiation source (Kyoto, Japan). All pH measurements were carried out by 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). 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 BAHR-Thermo analysis GmbH (Hüllhorst, Germany) under air atmosphere at the heating rate of 10 ˚C/min. The X-ray diffraction (XRD) patterns was achieved on a Philips-PW12C diffractometer (Amsterdam, The Netherlands) with Cu Kα radiation.

2.2. Chemicals and reagents

All reagents were of analytical grade were purchased from Merck (Darmstadt, Germany). A 1000 mg L^{-1} standard solution of Cd(II), as well as HCl, HNO_3, N $(CH_2CH_3)_3$, toluene, acetonitrile, 2-aminobanzothiazol, $FeCl_3$, $FeSO_4$, NaOH, NH_4OH (32 % solution), azobisisobutyronitrile (AIBN), ethylene glycol dimethacrylate (EDGMA), 3-Choloro1-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 was 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.

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2.3. Procedures

2.3.1. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 NPs were synthesized according to the previously reported procedure [33]. 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 NPs was confirmed by IR spectroscopy and X-ray powder diffraction.

2.3.2. Preparation of vinyl functionalized Fe_3O_4

Vinyl functionalization of Fe_3O_4 NPs was performed by reaction of silane agents with Fe_3O_4 NPs according to the recent report [39]. To prepare vinyl functionalized Fe_3O_4 NPs, 1.0 g of prepared Fe_3O_4 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 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 metals determination [40]. On this step vinylated ligand was prepared by the reaction of 2-aminobanzotiazol as a ligand (1 mmol) and of 3-choloro1-propen (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 Fe_3O_4@IIP nanosorbent

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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 Fe_3O_4 were dispersed in 100 mL of methanol, then, the mixture temperature was raised to 70 ºC 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 template (cadmium ions) was removed by a solution containing 1 mol L^{-1} HCl.

In order to confirm the removal of Cd(II) ions, the small amount of magnetic polymer was treated by piranha solution, then Cd(II) ions was determined by FAAS. Piranha solution, containing concentrated H_2SO_4 and 30% solution of H_2O_2 (3:1 v/v), dissolves the polymer network as well as Fe_3O_4 NPs and releases metallic ions in solution, which can be determined by FAAS [39]. It's important to remark that this process was performed just on 20 mg of polymer as a trial experiment to confirm that an efficient removing of Cd (II) ions template by acidic elution was accomplished. Therefore, the results showed that eluting by 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 magnetic IIP is shown in Fig. 1.

2.4. Extraction procedure

The extraction procedure consists of two steps: in the sorption step, pH of sample solution was adjusted at 7.0, then, 20 mg of 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. Concentration of cadmium ions in the eluent were evaluated by FAAS.

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2.5. Real samples

The urine samples were obtained from workers employed in one of automobile industries (Tehran, Iran). The samples were collected in sterile sample containers and were kept in the refrigerator (4ºC). 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 HNO_3 (1% v/v) and 2 mL of H_2O_2 (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 Cd(II) content in urine samples, 20 mg of prepared sorbent was weighted 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 Fe_3O_4 NPs surface with vinyl groups was carried out through the direct method for functionalization of Fe_3O_4 with triethoxysilan agents reported before [8]. The reaction of vinyl functionalized Fe_3O_4 with vinylated ligand complex as another monomer in the presence of Cd(II) as a template, AIBN as an initiator and EGDMA as the cross linker cause 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 IIP showed 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

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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 ºC. Nevertheless, according to the loss of 20 % of the composite weight, it can be concluded that the composite was burned causing 20% loss of its weight. This reduction was belonging to the polymer and residue was contributed to Fe_3O_4. In addition, the size and morphology assessment of synthesized sorbent were confirmed by SEM (Fig. 2-a,b). By investigating these micrographs, it was becoming apparent that the sorbent consists of spherical NPs with approximately 40 nm in diameter. It is worth mentioning that, since the magnetic NPs are coated with polymer, they will not be destroyed in acidic solutions [9].

According to the XRD pattern, the Fe_3O_4 structure remained unchanged after polymerization; it means that, the Fe_3O_4 did not decompose or convert to Fe_2O_3. Also, according to the Fig. 2-c, and the Scherrer equation, the broad peaks in the XRD pattern show that, Fe_3O_4 is in nanosized scale. The average crystallite size of magnetic IIP 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, 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 magnetic IIP was computed from XRD pattern and found to be about 28 nm. The XRD pattern of Fe_3O_4@IIP showed that, length of peaks reduced compared Fe_3O_4 XRD pattern. It can be concluded that, Fe_3O_4 nano particles have been coated with polymer compounds.

3.2. Optimization of the preconcentration method

3.2.1. Effect of sample pH

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The pH factor has ability to change the coordination sites of the ligand, so, it will be one of the most controlling parameters for sorption of Cd(II) on 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 by 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). Optimized sample pH for adsorption of Cd(II) onto 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) ions sorption. Moreover, in the alkaline pHs, the Cd(II) precipitate 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 IIP, HCl was chosen among H_2SO_4, HNO_3 and HCl. The inspection of the effect of eluent volume on the recovery of Cd(II) showed that, 4.0 mL of the 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 extraction of cadmium.

3.2.3. Optimization of sorption and elution time

Effect of time is one of the important factors in the analytical process while the inadequate time reduces the procedure efficiently and extra times cause lowering 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 magnetic IIP was suspended to the solutions and stirred for various durations and at the end of this process was washed with 5.0 mL distillated water. Then, the sorbent was separated by placing a magnet and the pre-concentrated analyte was determined by FAAS after eluting by 2 mol L^{-1} HCl. According to the Fig. 3, both optimized

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sorption and elution time 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. Compare to 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 decreasing of 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 contained, individually the interfering ions, Na^{+}, Pb^{+2}, Zn^{2+}, and Cu^{2+} were analyzed under the optimum condition. Also the X ions 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 signal compared to the signal of Cd(II) ions without any interference [9]. As shown in Table 1S, none of these ions do not 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; Although IIP can be considered as an SPE procedure, based on the results obtained in this study, IIP is promising to be more selective. The phase can be synthesized in a short time followed by a simple protocol for extraction stage, making method to be more convenience compare to the usual silica based SPE technique.

3.3.1. Analytical figures of merit

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In order to prove the precision and accuracy of the present technique, reproducibility of the optimized method was validated for day-to-day and within-day reproducibility using spiked aqueous samples. 25 mL samples were used at low, medium, and high concentrations of 2, 10, 50 µg L^{-1} respectively. A linear standard curve was obtained for extracting samples over the range concentrations every day 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 from day-to-day and within-day. Coefficient of variations (CV%) of 0.092, 0.064, and 0.017 were obtained for 2, 10, and 50 µg 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 standard addition method and a linear curve was plotted (R^2>0.98).

3.3.2. Method validation

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

3.3.3. Determination of urinary cadmium

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

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According to the available researches, analytical performance of those methods which were used specific instrument like graphite furnace atomic absorption spectrometry (GFAAS) or electrothermal atomic absorption spectrometry (ETAAS) are better than FAAS; 0.09, 0.045 and 5.75 μg L^{-1} respectively. Utilization of preconcentration techniques can cause increasing the performance of analytical method even has done by FAAS.

This method already had not been used for extraction of metallic ions through urine samples. Furthermore, according to the ATSDR profile of Cd(II), the lowest LOD for determination of Cd(II) by FAAS method was 5.67 μg L^{-1} [42], in which, obtained LOD of the present study was 0.6 μg L^{-1} (Table 3). Excellent sensitivity of magnetic IIP extraction allows researchers to determine trace concentration of Cd(II) in urine samples. Also, there is no need to use instruments like Graphite furnace atomic absorption Spectrometry (GFAAS) or Electrothermal Atomic Absorption Spectrometry (ETAAS) in similar studies. In the other hand measuring of Cd(II) by Fe_3O_4@IIP needs no pretreatment like acidic digestion, filtration, or centrifuge.

4. Conclusion

A new magnetic ion imprinted (IIP) polymer has been synthesized by the coating an IIP on the surface of Fe_3O_4 nanoparticles to achieve highest surface area for extraction aims. 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 achieved, i.e. pH = 7.0, sorption and elution time 5.0 min, eluent volume 4.0 mL (2 mol L^{-1} HCl). The high selectivity of this magnetic IIP can determine Cd(II) in biological samples without the need of unintelligible instrument like GFAAS or ETAAS, causing reduced expenses as well as saving time. Other advantages of this method are: low time-consuming due to the

Analytical Methods Accepted Manuscript

magnetically-assisted separation of the sorbent and high surface area; therefore, satisfactory results can be achieved using fewer amounts of the sorbent. On the other hand, according to day-to-day and whiten-day reproducible experiments, this technique gain an acceptable reliability degree for analyzing biological samples.

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Analytical Methods Accepted Manuscript

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

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Table 2

Measurement of Cd(II) in urine samples by using 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

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Table 3

Comparative LOD of various methods for determination of Cd(II) in urine samples.

Type of samples	Preparation method	Analytical method	LOD ($\mu g\ L^{-1}$)	Ref.
Urine	Modification of 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	Fe_3O_4@SiO_2 Cd^{2+}	ETAAS	0.19	[17]
Urine	Fe_3O_4@IIP Cd^{2+}	FAAS	0.6	This study

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Figure captions:

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

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

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).

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Fig. 1

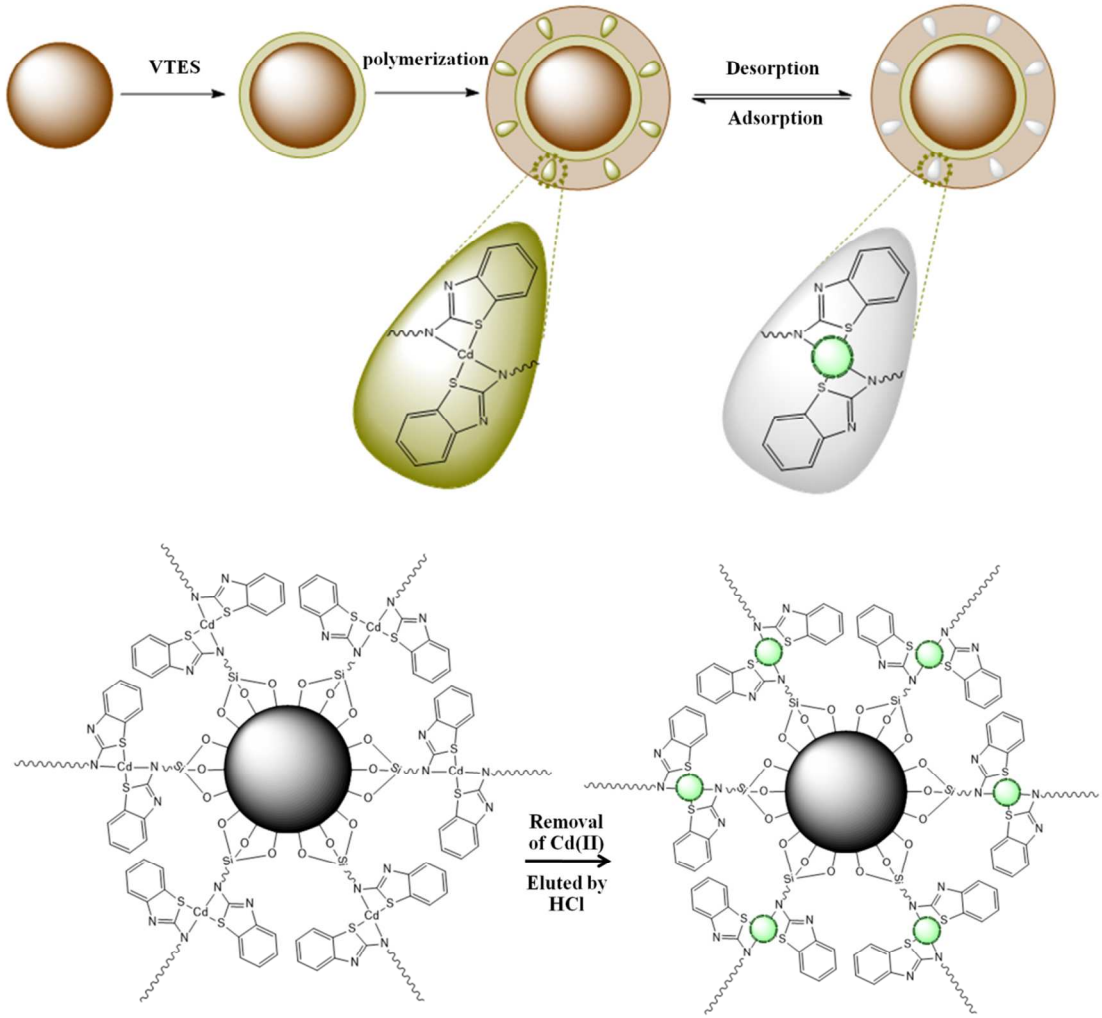

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Fig. 2

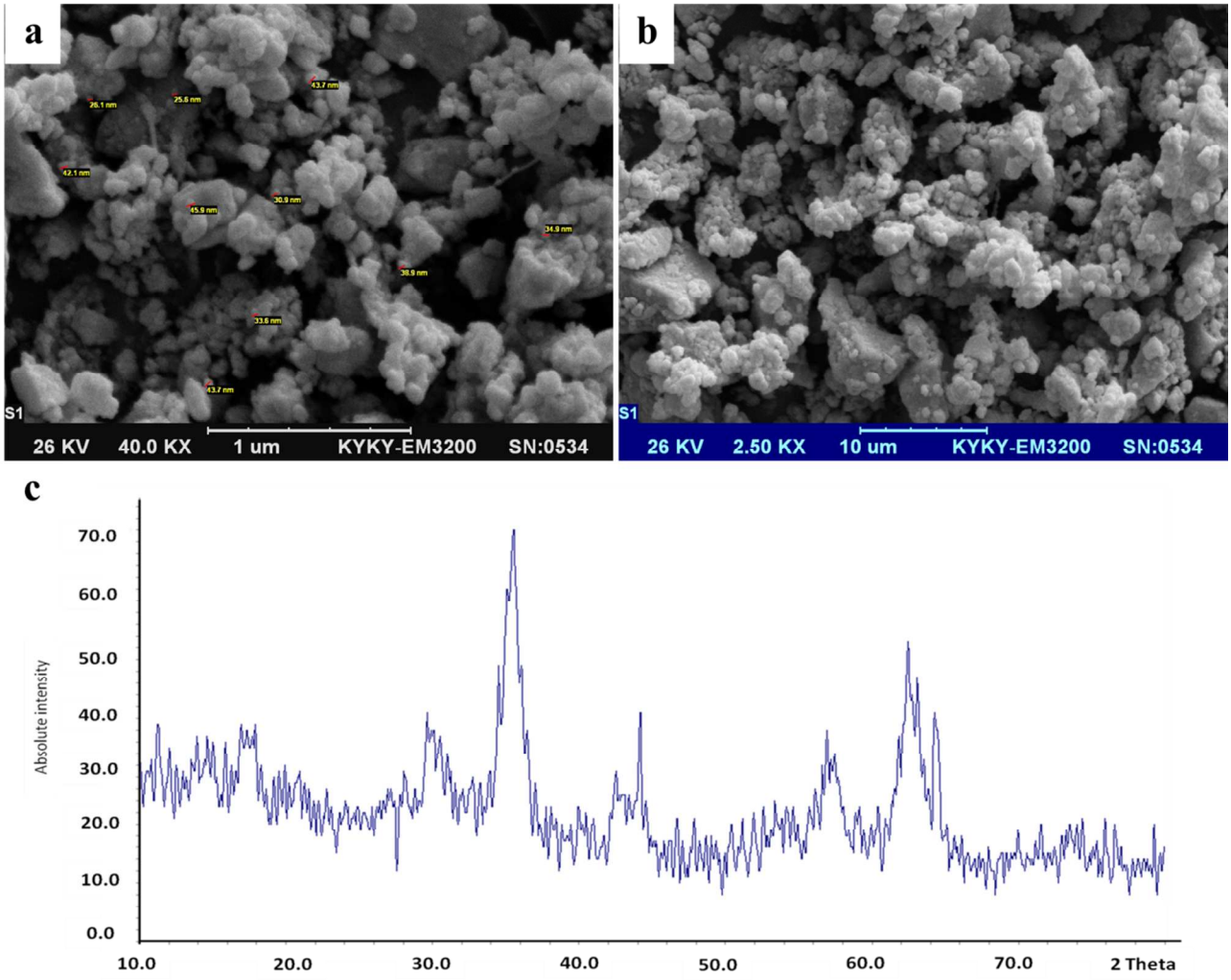

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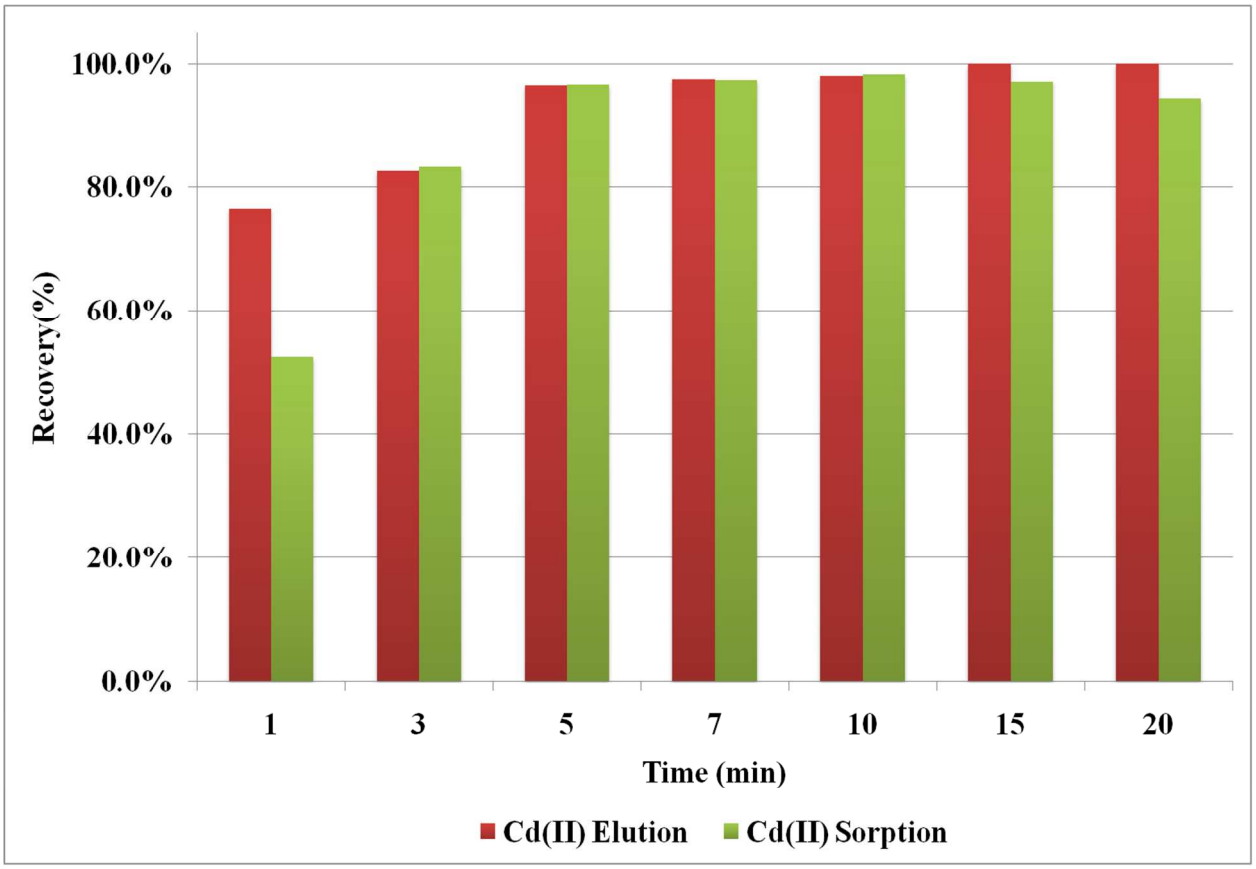
Fig. 3



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