



A Simple and Fast Method Based on New Magnetic Ion Imprinted Polymer as a Highly Selective Sorbent for Preconcentration and Determination of Cadmium in Environmental Samples

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Abstract

Background: The analysis of heavy metals at trace level is one of the main toxicologists concern, due to their vital rules in human's life. Cadmium is one of these toxic heavy metals, which released to the environment from various industries.

Methods: In order to determine Cd (II) ions in various matrices magnetic ion-imprinted polymer (IIP) method has been developed and applied. This nano-sorbent has been synthesized by coating an IIP compound on Fe₃O₄ nanoparticles core to achieve highest surface area. This polymer has been used to evaluate Cd (II) levels in food, river, and wastewater in Tehran, Iran.

Results: Fe₃O₄@Cd-IIP was stable up to 300 °C. The various factors such as sample pH (optimized as 7), elution/sorption time (5 min), eluent amount (4 mL HCL), and its concentration (2 mol L⁻¹) were optimized. Analysis instrument in all steps was Flame Atomic Absorption Spectrophotometer (FAAS). In this study, the detection limit was determined down to 0.6 µg L⁻¹.

Conclusion: This method was applied successfully for the preconcentration and determination of Cd (II) ions in environmental samples obtained from rivers, various foods and wastewater. In addition, the accuracy of the method was confirmed by analyzing a certified reference material (Seronom LOT NO2525) and spiked real samples.

Keywords: Cd (II), Magnetic ion imprinted polymer, Selective extraction, Environmental samples

Introduction

As industries are extensively developed, large amounts of heavy metals are released more into the environment causing serious environmental pollution and threaten animals as well as human health, even at low concentrations. The analysis of heavy metals at trace levels is one of the most important environmental toxicologists concerns, due to their vital rules in human's life. Cadmium,

as a heavy metal, appears in the environment due to industrial processes such as coal and oils combustion, smelting, mining, and alloy processing. Cadmium can be located in the kidneys and damages their filtering function. Furthermore, it can be preserved in human organs for a long time (1, 2). However, because of low concentration and matrix effect, various separation and pre-

concentration methods are used prior to its determination. Different treatment methods such as liquid-liquid extraction, solid-liquid extraction (3), liquid-phase Micro-extraction (4), solid-phase micro extraction (5), molecular imprinted polymer phase extraction (6-10), solid-phase extraction (11-14), cloud point extraction (15), coprecipitation (16) and various technique like flame atomic absorption spectrometry (17) and graphite furnace atomic absorption spectrometry (18) have been used for determination of cadmium in the environmental samples. One of the frequently used techniques among these methods is solid phase extraction (SPE). SPE is a simple, fast and relatively cheap technique for determination of heavy metals (19, 20). New sorbent based on ion-imprinted polymer (IIP) has recently been developed along with special properties resulting in selectivity and sensitivity of sorbent (21). IIPs have specific sites with high selectivity and affinity for the target metal ions. Ion imprinting has been synthesized by polymerization reaction between functional and cross-linking monomers in the presence of the template (22).

Recently, imprinted polymer equipped with magnetic particles (M-IIP) has attracted much more attention. Compared to the conventional imprinted polymers, because of nano particles, magnetically imprinted polymers have large surface area and high extraction efficiency and therefore, fast extraction dynamics can be achieved by using such sorbent (23, 24). Nowadays, techniques combining Fe_3O_4 particles with different sorbents for extracting metal ions from complex matrix have been developed (25).

In this study, magnetic ion imprinted polymer has been synthesized as a new sorbent for extraction and preconcentration of Cd (II) from real samples including food, industrial waste, and rivers, followed by its determination by FAAS.

Methods

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 Cd (II). 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 transforms infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Bruker IFS-66 FT-IR Spectrophotometer (Massachusetts, USA). Morphology and size of the magnetic IIP were observed on a Philips Scanning electron microscope (XL-30, Almelo, and The Netherlands). The thermal gravimetric and differential thermal analysis (TG-DTA) was carried out on a BAHRTHERMO analysis GmbH (Hüllhorst, Germany) under air atmosphere at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The X-ray diffraction (XRD) patterns were achieved on a Philips-PW12C diffractometer (Amsterdam, The Netherlands) with Cu $K\alpha$ radiation.

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 , $\text{N}(\text{CH}_2\text{CH}_3)_3$, toluene, acetonitrile, 2-aminobanzothiazol, FeCl_3 , FeSO_4 , NaOH, NH_4OH (32 % solution), azobisisobutyronitrile (AIBN), ethylene glycol dimethacrylate (EDGMA), 3-Choloro-1-propene and trimethoxy vinyl silane were purchased from Merck (Darmstadt, Germany). 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.

Synthesis of magnetic ion imprinted polymer

Fe_3O_4 NPs were synthesized according to the previously reported procedure (22). Briefly, 10.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4.0 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 100 mL of deionized water, degassed with nitrogen gas for 15 min and heated to $80\text{ }^\circ\text{C}$.

Then, 15 mL of NH_4OH (32 % solution) was added drop wise 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. In the next step, vinyl functionalization of Fe_3O_4 NPs was performed (24). 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 h. Simultaneously, the vinylated ligand was prepared by reaction of 2-aminobanzotiazol as a ligand (1 mmol) and of 3-choloro1-propen (1 mmol) in 50 mL solutions of triethylamine and methanol (1:4 v/v) at room temperature. After 4 h the solvent was removed under the reduced pressure.

Then, one mmol of the vinylated ligand 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°C and afterward 0.08 g of AIBN and 1.1 mL of EGDMA were added. The composite was separated by a magnet, and after 48 h the template was removed by a solution containing 1 mol L^{-1} of HCl . Finally, the formation of this IIP was confirmed by IR spectroscopy, TG/DTA analysis, XRD and SEM.

Extraction procedure

The extraction procedure consists of two steps: in the sorption step, pH of the sample solution was adjusted at 7.0, then, 10 mg of magnetic IIP was suspended in the aqueous solution containing 1 mg L^{-1} of Cd (II) and stirred for 5.0 min. In desorption step, elution of adsorbed Cd (II) ions was performed by 4.0 mL of 2 mol L^{-1} HCl solution. After 5.0 Min, the concentration of Cd (II) in the eluent was determined by FAAS.

Preparation of certified reference materials and real samples

Fruit and vegetables samples

The fruit samples including Fenugreek, Cantaloupe, cucumber skin and green beans were collected from Tehran fields (Shahriyar-Tehran). The fruit samples were put in the cleaned polyethylene bags. After delivery to chemistry labora-

tory, each sample was washed with distilled water thoroughly, and then the samples were dried at 100°C for about 2 d. For the preparation of spiked samples, 1.0 mL of the standard working solution was added to 1.0 g of each sample. They were then allowed to stand at room temperature for the evaporation of the solvent; therefore, the equilibration between the analyses and the fruit samples was achieved. After grinding the dry fruit and vegetable (spiked or non-spiked), microwave-assisted acid digestion was carried out by adding 2mL of distilled water, 4 mL of nitric acid 65%, and 2 mL of hydrogen peroxide 33% (w/v) to 0.5 g of each sample (22). The reactors were then subjected to the microwave program (2.5 min at room temperature, 6 min at 140°C , and 5 min at 200°C in power of 550 W). When acid digestion was complete, the acid digests were diluted up to 25 mL with distilled water and kept in a refrigerator before magnetic solid phase extraction.

Wastewater samples

The wastewater sampling was done from the radiology waste of a hospital and waste of washing of painting process in an automobile industry in Tehran, Iran. Samples were collected in clean and vacuumed glass bottles. No pretreatment has been carried out in order to evaluation of Cd (II) by the mentioned method in this study.

River Water samples

The water sampling was done from the various zones of Iran; including Tehran, Kermanshah and Ilam cities. In this study, tap water and rivers were examined. Samples were collected in clean and vacuumed glass bottles.

Reference material

The concentration of Cd (II) ions was determined at optimum conditions in certified reference materials (Seronorm LOT NO2525). Seronorm LOT NO2525 certified was digested according to the mentioned procedure for fruit and vegetable samples. The pH of the solution was adjusted to 7.0 for the separation and pre-concentration of Cd (II) ions from the solution.

Ultimately, the preconcentration procedure was applied to the resulted solutions.

Results

Sorbent characterization

Formation of Fe_3O_4 NPs has been identified by FT-IR, SEM and XRD. The synthesized imprinted polymer was characterized by IR spectroscopy, scanning electron microscopy (SEM), thermo gravimetric and differential thermal anal-

ysis (TG/DTA). 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}). However, the thermal stability of this nano-composite was determined up to $300\text{ }^\circ\text{C}$ according to the TG/DTA analysis. Also, the nano surfaces and sorbent's morphology were confirmed by SEM (

Fig. 1, a-b) and XRD (

Fig. 1, c).

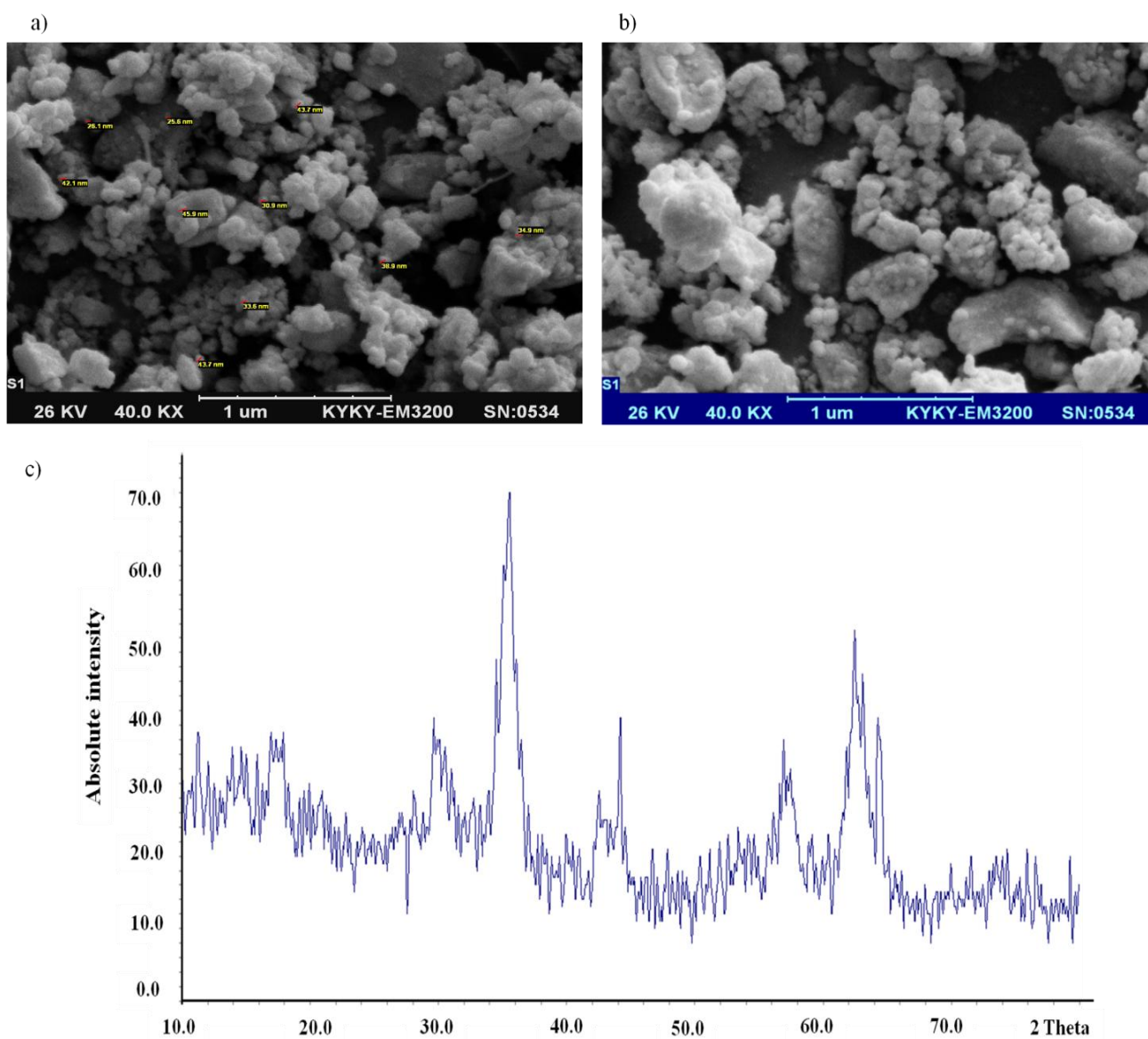


Fig. 1: (a) and (b) SEM micrographs of synthesized magnetic IIP; (b) XRD pattern of magnetic IIP

Optimization of the preconcentration method

Effect of sample pH

To achieve the optimized sample pH condition during the extraction process of sample solutions containing 0.5 mg L^{-1} of Cd (II), pH adjusted in the range of 3.5-8. After stirring for 5 min, the adsorbed Cd (II) ions were eluted by 4.0 mL of 2 mol L^{-1} of HCl, subsequently, the amount of Cd(II) ions in the eluent were determined by FAAS. Optimized sample pH for adsorption of Cd (II) on this compound was 7.0.

Effect of eluent type, volume and its concentration

In order to elution of Cd (II) from IIP, HCl was selected between H_2SO_4 and HNO_3 . 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} of HCl is the optimum volume for desorption

of Cd (II) ions. Therefore, to obtain higher preconcentration factors, 4.0 mL of 2 mol L^{-1} HCl was selected in this work. In the batch method, solid phase was separated by the magnet (1.4 Tesla).

Optimization of sorption and elution time

In order to evaluate the effect of time, 25 mL of solutions containing 0.5 mg L^{-1} of Cd (II) were adjusted to pH=7.0 and 10 mg of magnetic IIP were suspended to the solutions and stirred for various durations. At the end, the sorbent was separated by placing a strong magnet and the preconcentrated analyte was determined by FAAS after eluting by 2 mol L^{-1} HCl. According to

Fig. 2, 5.0 min were chosen for both optimized sorption and elution times.

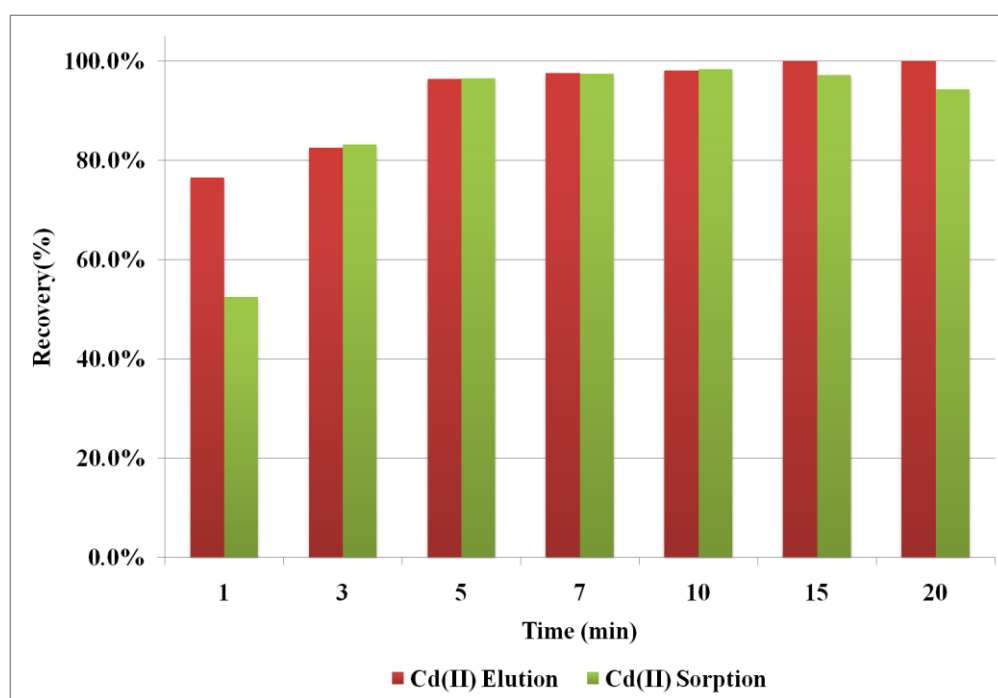


Fig. 2: Effect of sorption and elution times on the recovery of Cd (II)

Potentially influence of interfering ions

In order to investigate the selectivity of the sorbent, the effect of four cations was assessed. For

this purpose, 0.5 mg L⁻¹ Cd(II) ions solutions contained individually the interfering ions, Na⁺, Pb⁺², Zn⁺², and Cu⁺² were analyzed under the optimum condition. The tolerable amount was defined as the maximum concentration causing a change of less than 5% in signal compared to the signal of each ion without any interference (24). None of these ions do interfere with the concentrations encountered in aqueous samples.

Analytical figure of merit

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 extracted sample over the range concentrations every day for 6 consecutive days

(n=6) with the correlation coefficient of 0.997 or greater (Table 1).

Method validation

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.

Real environmental samples analysis

The mentioned method was applied for determination of Cd (II) ions concentration in food samples, rivers water, and industrial wastes. After sample preparation, each sample divided into 4 parts. Subsequently, by adding 10 mg of prepared sorbent under the optimized condition and by consequently using standard addition method Cd (II), levels were evaluated in each sample. The results have been presented in Table 2.

Table 1: Day-to-day (D-day) and within day (W-day) reproducibility of cadmium determination in aqueous sample. Sample volume 25 mL, N = 6

Statistical data	Concentration added (µg L ⁻¹)					
	2		10		50	
	D-day	W-day	D-day	W-day	D-day	W-day
Mean	4.63	3.49	11.76	11.29	50.91	50.69
SD	0.43	0.51	0.79	0.66	0.88	0.70
CV(%)	0.092	0.146	0.064	0.058	0.017	0.014

Table 2: Measurement of Cd (II) in environmental samples by using Fe₃O₄@IIP

Sample	Sampling place	Sample name	Concentration of Cd(II) (µg L ⁻¹)
1	Tehran, Iran	Tap water	0.0
2	Tehran, Iran	Baghefeiz river	6.6
3	Kermanshah, Iran	Bisooton river	6.2
4	Ilam, Iran	Seymareh river	12
5	Tehran, Iran	Waste of washing of painting process in an automobile company	15.7
6	Tehran, Iran	Radiology waste of a hospital	21.3
7	Tehran, Iran	Cucumber Skin	47.0
8	Tehran, Iran	Cantaloupe	1.5
9	Tehran, Iran	Green beans	15.7

10	Tehran, Iran	Fenugreek	52.5
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Discussion

Sorbent characterization

According to the FT-IR plot, both spectra before and after Cd (II) leaching are structurally same, but because of metal leaching from IIP mentioned band raised. Important band regarding metal banding in the presence of Cd (II) is 1145 (C=S), 1629 (C=N), and 3415 (N-H) cm^{-1} . For leached polymer, they raised as 1149, 1632, and 3437 cm^{-1} respectively.

Besides, Fe_3O_4 @Cd-IIP was stable up to 300 °C. Nevertheless, according to 20% loss of the composite weight, 20% of this sorbent is consists of polymer burned at high temperature and the rest of mass was Fe_3O_4 . By extracting of SEM, the sorbent can be consisted of spherical nanoparticles with more or less than 40 nm in diameter. Since the magnetic nano-particles are coated with polymer, they will not destroy in acidic solutions (24).

According to the XRD pattern, the Fe_3O_4 structure remained unchanged after polymerization; the Fe_3O_4 did not decompose or convert into Fe_2O_3 . However, according to the

Fig. 1-c, as well as, the Scherrer equation, the broad peaks in the XRD pattern showed that, Fe_3O_4 is at 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. 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, the length of peaks has been reduced comparing Fe_3O_4 XRD

pattern. Fe_3O_4 nano particles have been coated with polymer compounds.

Optimization of the preconcentration method

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 adsorption of Cd (II) on the synthesized polymer. According to the pH optimization tests, optimum sample pH was 7.0. This is because at low pH values, an excessive protonation of the lone pair of electrons on nitrogen and sulfur can be seen, resulting in the decrease of the Cd (II) ions sorption (25). Moreover, in the alkaline pHs, the Cd (II) precipitate as $\text{Cd}(\text{OH})_2$ may cause decreasing in removal efficiency (22).

The volume of 4 mL of elution showed that high concentration factor for cadmium ions and cause reduce solvent usage. Interestingly, at larger volumes, the recoveries were not significantly raised by increasing the eluent volume. Also according to the elution type selection HCl has prepared more recoveries.

Time of sorption and desorption which have a strong influence on extract procedure efficiency were investigated as the insufficient time reduces the procedure efficiently and extra ones cause waste time. The result of tests showed that 5.0 min was the optimum time for both factors. This fast extraction and elution duration could be attributed to the high surface area dealing with these IIP nano-particles. Batch extraction techniques will reduce these factors. Fast extraction and elution duration could be attributed to the high surface area dealing with these IIP nanoparticles (10). Compared to the column technique, batch method takes shorter sorption and desorption times (23).

Potentially influence of interfering ions

In order to accurate evaluation of Cd (II) in environmental samples, interfering factors such as complex matrices or unknown concentrated in-

terfering ions should be removed or reduced. Cadmium and other ions may be released into rivers by natural or industrial activities. Due to this fact, the used sorbent should be selective enough to extract Cd (II) in the presence of other material especially metallic ions, which cause a decrease in recovery. The method of extraction is enough selective to measure an accurate value of Cd (II) even in complex matrices. This high selectivity could be attributed to the highly selective sites, the size, and shape was specifically fitted to the Cd (II) ions. Therefore, the method was selective toward the Cd (II) extraction at pH=7. Furthermore, extraction is not affected by high concentrations of Na ions, which are may exist on earth.

Method validation

According to the table 1 in within-day experiments evaluation, six experiments were performed each day for three consecutive days. The extraction procedure was reliable and reproduc-

ible from day-to-day and within-day (13). The coefficient of variations (CV%) of 0.092, 0.064, and 0.017 was 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 (11). Also compare to the reference material the result have good agreement whit certified material. Furthermore, according to the ATSDR profile of Cd (II) the lowest LOD of determination of Cd (II) by ASS in environmental samples is 10 $\mu\text{g L}^{-1}$ (26), While, LOD of this study obtained down to 0.6 $\mu\text{g L}^{-1}$ (Table 3). High selectivity and appropriate preconcentration of this method allow the environmental analyst to determine the low concentration of Cd (II) in various samples without the need for instruments like GFAAS or ETAAS. In addition, evaluating of Cd (II) by $\text{Fe}_3\text{O}_4\text{@IIP}$ method needs no pretreatment experiments like acidic digestion, filtration or centrifuge for semi-clear samples like waste or river water (27).

Table 3: Comparative of LOD of a various method for determination of Cd (II) in environmental samples

Type of samples	Preparation method	Analytical method	LOD	Ref.
Water and wastes	Digestion with acid	ICP-MS	1 ($\mu\text{g L}^{-1}$)	(28)
Water and wastes	Digestion with HCl and HNO_3	AVICP-AES	0.1 ($\mu\text{g L}^{-1}$)	(29)
Water and sediments	With no preconcentration or pretreatment	AAS	10 ($\mu\text{g L}^{-1}$)	(30)
Various	Direct aspiration with no preconcentration or pretreatment	AAS	10 ($\mu\text{g L}^{-1}$)	(30)
Food	Dry ashed; complexation with APCD; extraction with isoamyl acetate	AAS	0.1 (ng g^{-1})	(31)
Fruit	Homogenized fruit slurried with zirconia	ETAAS	0.3 (ng g^{-1})	(32)
Various	Preconcentration by $\text{Fe}_3\text{O}_4\text{@IIP}$	FAAS	0.6 ($\mu\text{g L}^{-1}$)	(This study)

Conclusion

The novel magnetic IIP has been synthesized by coating an IIP on Fe_3O_4 nanoparticles for the achievement of the highest surface area for extraction aims. Selectivity of this ion imprinted polymer has made it be a suitable and selective

sorbent for extraction and preconcentration of Cd (II) in various environmental samples. The best performance by least expenses, optimum parameters achieved i.e. pH=7, sorption and desorption time 5 min, elutant 4mL (2M HCl). The high selectivity of this IIP against Cd (II) can determine this ion in environmental samples as fast

and easy as possible without unintelligible instrument like GFAAS or ETAAS causing reduce expenses as well as saving time. On the other hand, according to day-to-day and white-day reproducibly experiments, this technique gains acceptable reliability degree for analysis of environmental samples.

Ethical considerations

Ethical issues (Including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc.) have been completely observed by the authors.

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