Synthesis and application of a novel magnetic nanocomposite for determination of trace Cd(II) in water samples

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ABSTRACT

In this work for the first time, Fe_3O_4@SiO_2 core-shell nanoparticles functionalized with isatin groups as a magnetic nanosorbent was applied for the simultaneous extraction of trace amounts of cadmium (II). The characterization of this nanosorbentwas studied using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The effect of several factors such as pH, amount of sorbent, extraction time, type and volume of the eluent, sample volume, and sorption capacity. In the selected conditions, it was observed that the limits of detection were 0.11 ng mL^{-1} for Cd(II) and the maximum sorption capacity of this suggested magnetic nanosorbent was 120mg/g. Finally, the suggested procedure was applied for determination of cadmium (II) at trace levels in different water samples with satisfactory results.

Keywords: Magnetic nanosorbent, Isatin, Cadmium (II), Solid phase extraction

1. INTRODUCTION

One of the main problems in environmental pollutants is heavy metal ions, which have toxic effects on the human health and life in aquatic systems. Therefore, one of the greatest interested subjects by analytical chemists is determining the trace amounts of heavy metals and this is one of the important subjects in analytical chemistry [1]. The trace amount of heavy metals are the most important contaminants in the source water. The presence of metallic materials in natural source water was enhanced as a result of growing the application of heavy metals in industries and causes several environmental problems [2].

Recent years, nanoparticle materials, especially magnetic nanoparticles have aroused a great deal of attention in analytical chemistry as the sorbents [3-5]. In contrast, iron oxide nano-particles due to the important properties such as the high surface area to volume, nano-size range and super-magnetism are suitable particles and in water treatments due to this propertiesare highly desirable [6]. Silica is one of the most ideal compositions to be used as a shell.The silica shell protects Fe_3O_4 NPs in acidic medium which is necessaryfor elution of most metal ions. Also, silica surface with silanol groups can react with silane coupling in order to conjugate with a variety of different ligands [7].

A number of preconcentration methodsfor preconcentration and detection of trace metal amounts have been gained attention nowadays, including solvent-assisted dispersive solid phase extraction [8], solid phase extraction (SPE) [9], magnetic solid phase extraction (MSPE) [10], electrochemical deposition [11], and membrane separation [12].

In the current research, for the first time, $Fe_3O_4@SiO_2$ core-shell nanosorbentwas modified with isatin($Fe_3O_4@SiO_2@Isa$) and used as a novel magnetic solid phase sorbent for removal and preconcentration of cadmium(II) and flame atomic absorption spectrometry (AAS) was chosen for monitoring the concentration of these target ions. The modified magnetic nanosorbent was synthesized by a simple reaction and characterized by Fourier transform infrared spectroscopy FT-IR, SEM, and XRD. The sorbent was then used to determine Cd(II) ionin different water samples and the obtained results was good.

2. EXPERIMENTAL
2.1. Reagents and materials

All reagents used in this study (NaOH, NH_3, HCl, HNO_3, H_2SO_4, isatine, 3-aminopropyltriethoxysilane (APTES), $Cd(NO_3)_2$, toluene, ethanol) were purchased from Merck (Darmstadt, Germany), Fluka (Buchs, Switzerland) or Sigma-Aldrich (Steinheim, Germany) without any further purification. Tetraethoxysilane, $FeCl_3.6H_2O$, $FeSO_4 \cdot 7H_2O$ were used in magnetic nanoparticles preparation and were purchased from Aldrich. The stock solution (1000 mg L^{-1}) was readied by dissolving suitable amounts of $Cd(NO_3)_2$, in de-ionized water.

2.2. Apparatus

Concentrations of target metal ions were performed with an Agilent Series AA (model 240 AA) flame atomic absorption spectrometer (FAAS) equipped with the air-acetylene burner. The FT-IR spectra (400–4,000 cm^{-1}) were recorded by S, 8400 Shimadzu FT-IR spectrophotometer. A scanning electron microscopy and (SEM) (KYKY, EM 3200) were used to analyze the surface morphology. X-Ray powder diffraction (XRD) patternswere performed using a Bruker D8 Advance (Germany) with the 2θ angle varying between 5 and 90° (λ=1.5).

2.3. Preparation of $Fe_3O_4@$ SiO_2 core-shell nanosorbent

Magnetic Fe_3O_4 nanoparticles (MNPs) were obtained based on simple chemical coprecipitation of Fe^{2+} and Fe^{3+} ions as reported elsewhere [13]. Briefly, 6.1 g of $FeCl_3.6H_2O$ and 4.2 g of $Fe_2SO_4.7H_2O$ [Fe (III)/Fe (II) molar ratio = 2/1] were dissolved in 100 mL distilled water, and heated at 80 °C for 30 min, then add 10 mL of ammonia solution (25 w/w%) drop wise until formation of Fe_3O_4 occurred. This system was mixed for 4 h by a magnetic stirrer in the nitrogen atmosphere. During the whole procedure, the temperature of the solution was hold at 80 °C. The product (Fe_3O_4 NPs) was effectively separated in few second by a strong magnet and repeated washing with distilled water thoroughly, and finally, the nanoparticles were vacuum-dried at 40 °C for 4 h. Next, the grafting procedure of magnetic particles with silica was accomplished as follows:

1 g of the prepared Fe_3O_4 NPs were dispersed via ultrasonic in a solution of 100 mL deionized water, 25 mL ethanol and 1.5 mL NH_4OH (25%). Then 3 mL TEOS was added dropwise to the solution under stirring until the process of magnetic particles with silica was accomplished [14]. After 12

h stirring at 40 °C, with help of the external magnet, the formed $Fe_3O_4@SiO_2$ NPs were collected and washed with deionized water and ethanol and then dried.

2.4. Functionalization of $Fe_3O_4@$ SiO_2 core-shell NPs

The procedure for functionalizing $Fe_3O_4@SiO_2$ core-shell NPs was performed in two steps as follows: In the first step, 1.0 g of $Fe_3O_4@SiO_2$ core-shell NPs was ultrasonically dispersed in 50 mL dried toluene in a three neck round bottom flask. Then 3-aminopropyltriethoxysilane (2.0 mL) was added to the solution inone portion after stirring for 1 h. The black solid was produced after refluxing under nitrogen atmosphere for 12 h. Afterward, $Fe_3O_4@SiO_2@APTMS$ core-shell NPs were isolated by the strong magnet and washed with water and ethanol several times until discard

any impurities, $GO@Fe_3O_4@APTMS$ nanoparticles were dried completely at 50 °C for overnight and were used in the next step of the experiment. The FT-IR spectrum, and SEM analyses were applied to confirm the synthesis of $GO@Fe_3O_4$ functionalized with APTMS [15].

In the second step, about 1.0 g of the $Fe_3O_4@SiO_2@APTMS$ core-shell NPs was dispersed in 50 mL toluene containing 1.0 g of isatinand the reaction mixture was stirred and refluxed for 24 h in an oil bath at 80 °C in the presence of nitrogen. Hereafter, the black solid obtained was successively collected by a strong magnet and washed with ethanol to remove excess unreacted materials and dried under vacuum at 40 °C overnight (Fig. 1). Then, FT-IR, SEM, and XRD were used for characterizing obtained $Fe_3O_4@SiO_2@Isa$ nanosorbent.

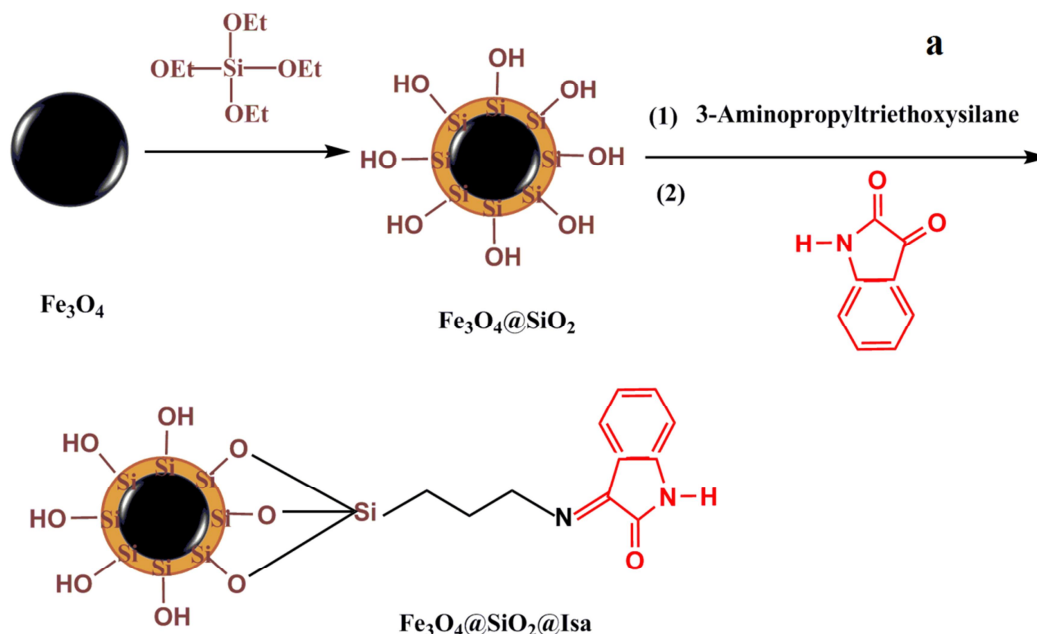**Fig. 1.** A schematic diagram for the synthesis of $Fe_3O_4@SiO_2@Isa$ nanoparticles

2.5. Real sample pretreatment

Presence of cadmium(II) ion in diverse samples such as water and vegetable

samples was determined by the $Fe_3O_4@SiO_2@Isa$ nanosorbent. Water samples, including, tap water (Tehran, Iran), and river water (Zayanderud,

Isfahan. Iran) were selectedfor evaluating the influence of the synthetic nanocomposite on the efficiency of the proposed approach, and then were filtered. 50 ml of each sample was adjusted to pH 6, and their cadmium(II) ion content was determined by the suggested extraction and preconcentration method.

2.6. Extraction procedure

For the extraction procedure, the pH of 10 mL aqueous solution including 0.5 mg L^{-1} of target ions was set at optimal pH (The solution pH was adjusted by dilute NaOH or HCl to desired value). Then, 20 mg of the dried magnetic nanosorbent was added into the solution and the prepared mixture was stirred for the suitable amount of time for ensuring adequate interaction between magnetic sorbent and ions. Afterward, the magnetic sorbent was collected from the solution with an appropriate magnet andthe concentrations of the metal ions in supernatant were directly determined by FAAS. In the elution step, 3 ml of 2mol L^{-1} HCl was used to elute the metal ions adsorbed on the sorbent. For this purpose, the mixture of sorbent and eluent was stirred for 5 min and then again exposed on the strong external magnet until obtaining the clear solution of eluent. Finally, the amount of analyts in eluent was determined by its injection into FAAS. It should be noted that the percentage of extraction for the employed samples was obtained using the following equation:

$$\%\text{Extraction}=C_a–C_b/\ C_a\times 100$$

where C_a and C_b are initial and final concentrations of each ion in the solution, respectively.

3. RESULTS AND DISCUSSION
3.1. Sorbent characterization

FT-IR spectrum of $Fe_3O_4$was recorded using the KBr pellet method. The advent of the absorption peaks at 582 cm^{-1} is ascribed to Fe–O stretching and the band at 3435 cm^{-1} is due to the intramolecular hydrogen bonding.The presented findings confirm that the synthesis of Fe_3O_4 NPs was performed successfully. For the $Fe_3O_4@SiO_2$ nanoparticles, the peaks at 1089 cm-1(Si–O–Si) and 798 cm-1(Fe-O-Si)attributed that SiO_2 was successfully coated on the surfaces of Fe3O4 nanoparticles.
For $Fe_3O_4@SiO_2@APTMS$ the absorption peak in the area of 1398 represents a Si-C group in the magnetic nanocomposite structure and the adsorption peak at 2900cm^{-1} (C-H) confirmed the existence of APTMS on the surface of $Fe_3O_4@SiO_2$ NPs. In FT-IR spectrum of $Fe_3O_4@SiO_2@Isa$ nocomposites, the absorption bands at 1400 and 1618 cm^{-1} areas represented the vibrational frequency of C=C and C=N band in $Fe_3O_4@SiO_2@Isa$, respectively. These observations indicate the modification of $Fe_3O_4@SiO_2$with Isa group [16]. The morphology of $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ nanocomposite func-tionalized with isatingroupwas studied using SEM for showing the morphology of the synthesized nanosorbents. Our literature survey at this stage revealed that according to SEM patterns shown in Fig. 2a and 2b reveal the obvious growth of nanocomposite particle size in $Fe_3O_4@SiO_2@Isa$ nanocomposite (the average size of $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2@Isa$ nanoparticles are about 27 and 48 nm, respectively).
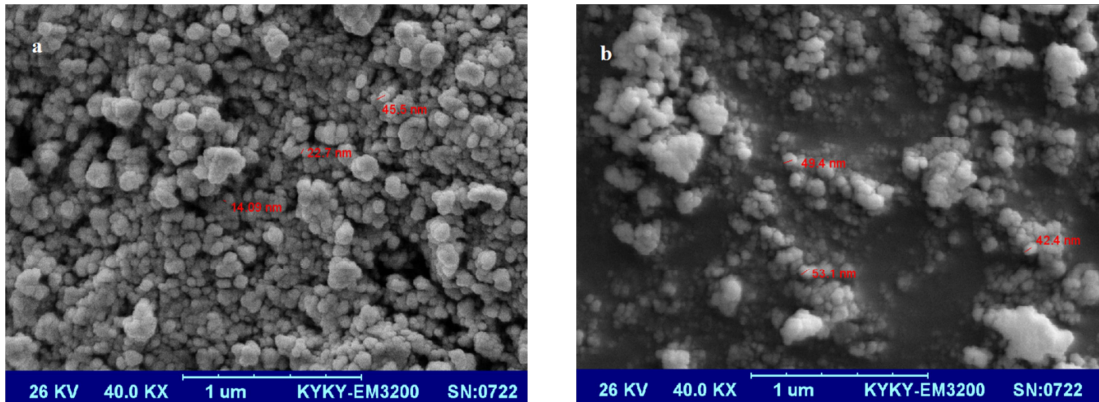
Fig. 2 The SEM image of (a) $Fe_3O_4@SiO_2$ (b) $Fe_3O_4@SiO_2@Isa$ nanocomposite

X-ray characterization: Fig. 3a and 3b shows XRD patterns of $Fe_3O_4@SiO_2$ nanocomposite and $Fe_3O_4@SiO_2@Isa$ nanocomposite after reaction of magnetic $Fe_3O_4@SiO_2$ with isatin group. Different peaks at 2θ = 30.1, 35.5, 43.2, 57.1 and 62.7 and the broad peak at 2θ= 20-30 (SiO_2 group) in Fig. 3b showed that structure of $Fe_3O_4@SiO_2$ nanoparticles remained intact after coating with Isa groups andany changes and decomposition occurring in the structure of $Fe_3O_4@SiO_2$ after modification(JCPDS No. 19-0629). The low-angle X-ray diffraction pattern of $Fe_3O_4@SiO_2@Isa$ showed decrease in intensity in peaks in comparison to unfunctionalized $Fe_3O_4@SiO_2$
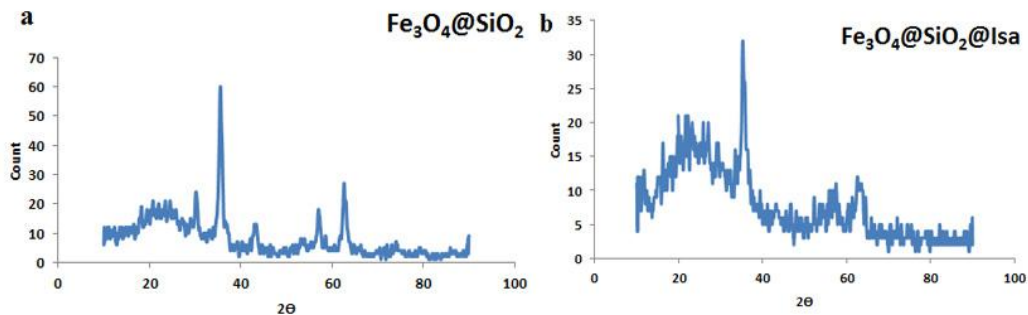
Fig. 3 The XRD pattern of (a) $Fe_3O_4@SiO_2$ (b) $Fe_3O_4@SiO_2@Isa$ nanocomposite.

3.2. Optimization of extraction conditions
3.2.1 Effect of pH

PH value is a crucial parameter in all extraction studies therefore it is crucial to evaluate the pH on Cd(II) sorption. To study this parameter, the pH of an aliquant of 100 mL sample solution including 1 mg L^{-1} of copper was adjusted and investigated in the range of pH 2–8. Then 20 mg of sorbent was added to the solution. The result depicted in Fig. 4 revealed that suitable recovery was achieved when the pH was 6. The uptake of recovery in acidic pHs was because of the oxygen and nitrogen groups protonation, which prevented their effective coordination to cadmium ions. Furthermore, the recovery decline in high basic pHs are mainly due to precipitation Cd^{2+} as $M^{n+}(OH)_n$.
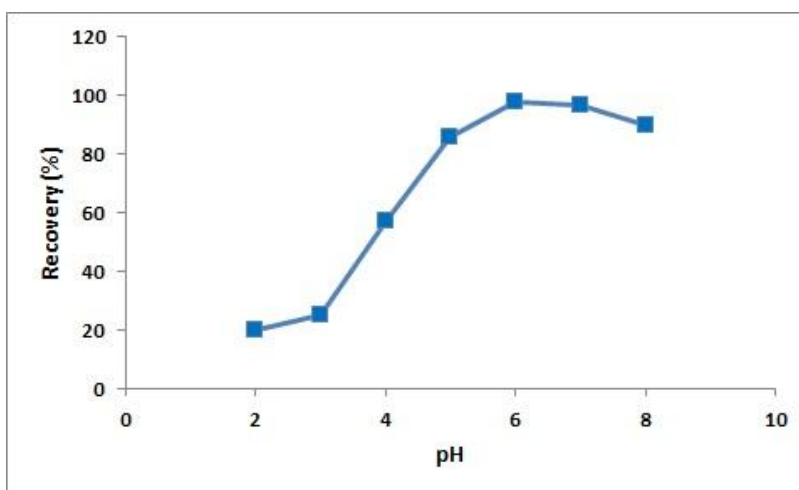
Fig 4. Influence of pH on recovery of Cd(II) ions on $Fe_3O_4@SiO_2@Isa$ nanocomposite.

3.2.2 Effect of nanosorbent amounts

For achieving the highest quantitative efficiency for extracting cadmiumions the optimal amount of $Fe_3O_4@SiO_2@Isa$ nanocomposite was obtained. Briefly, varying amounts of the nanocomposite powder ranging from 5–30 mg were tested. The results revealed that by increasing amounts of $Fe_3O_4@SiO_2@Isa$ nanocompositeup to 20 mg the extraction efficiency increased in response to the increase of surface area. Consequently, for the subsequent study 20 mg of nanocomposite was considered to be enough to achieve a satisfactory result.

3.2.3. Effect of sorption time

Different time periods (2, 4, 5, 8 and 10 min) for Cd(II) sorption on the magnetic $Fe_3O_4@SiO_2@Isa$ nano-composite was tested. For this step, 20 mg $Fe_3O_4@IIP$ was added to 100 mL

of sample solutions (1 mg L^{-1} of cadmium ion) at pH 6, and the mixture was shaken for different time periods. The sorbent was then removed using a suitable external magnet. For obtainingthe maximum yield,5 min is enough for extracting the analytes from solution quantitatively, and this time was selected as the optimum sorption time.

3.2.4. Elution condition

In the current study, several types of eluents (HCl, HNO_3, H_2SO_4, and EDTA) were selected for elution of Cd(II) ions from magnetic $Fe_3O_4@SiO_2@Isa$ nanocomposite and extraction procedure was performed. The obtained result indicated that the better eluent for Cd(II) from the sorbent was 3 mL of 2 mol L^{-1} HCl solution (Fig. 5).
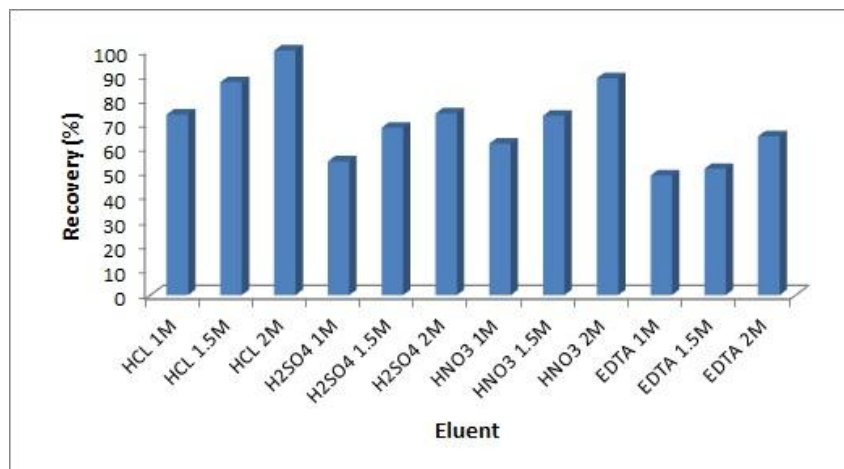
Fig. 5. Influence of eluent type and concentration on recovery of Cd(II) ion on
$Fe_3O_4@SiO_2@Isa$ nanocomposite.

3.2.5. Effect of sample volume

The volume of sample plays an important role in analyzing real samples and it is effective on the preconcentration factor. In a condition in which all solutions were adjusted according to the optimum condition obtained for the suggested technique, examination of the effect of sample volume parameter on quantitative sorption of Cd(II) was performed using 20 mg of $Fe_3O_4@SiO_2@Isa$ sorbent in various volumes of the sample within the range of 25-800 mL containing 1 mg of target ion. According to the results given in Fig. 6, the recovery of this ion on the $Fe_3O_4@SiO_2@Isa$ nanocomposite was obtained more than 98% for the sample volumes up to 600 mL, but it was reduced when dilutionwas raised up at higher volume. Thus, 600 mL of the sample volume was chosen for the proposed extraction method and the preconcentration factor (PF) for synthetic magnetic nanocomposite was calculated to be 200 when 3 mL of elution was used.
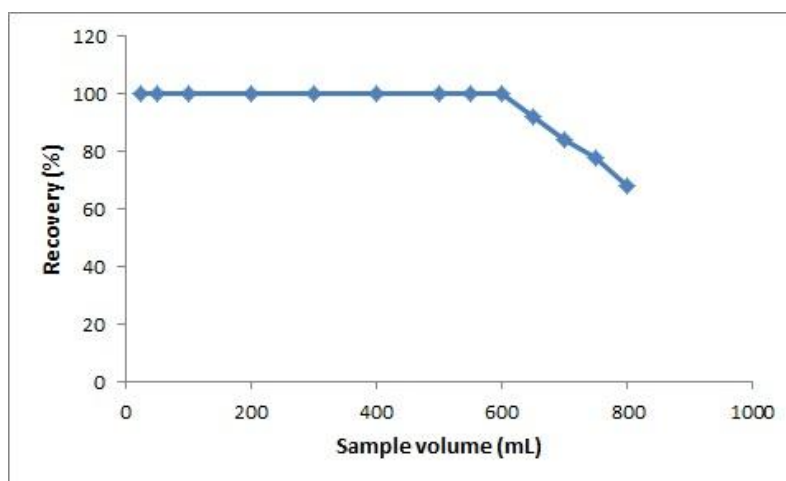
Fig 6. The effect of sample volume on recovery of Cd(II) ion on $Fe_3O_4@SiO_2@Isa$
nanocomposite.

3.3. Maximum adsorption capacity study

The total amount of every analytesorbed per gram of the magnetic sorbent is specified as the highest sorption capacity of the sorbent. To determine this parameter, the batch MSPE procedure was investigated using an aqueous solution containing 50 mg L^{-1} of Cd(II) ion and it was calculated by determining the difference between the concentration of analyte in the solution before and after extraction using FAAS.

The sorption capacity of magnetic $Fe_3O_4@SiO_2@Isa$ nanocomposite was calculated 120mg/g for Cd(II) ion. The sorption capacity of magnetic $Fe_3O_4@SiO_2@APTMS$ nanocomposite was calculated 60 that depicts better absorption by $Fe_3O_4@SiO_2@Isa$ nanocomposite.

3.4. Analytical performance of method

For this $Fe_3O_4@SiO_2@Isa$ nano-composite linearity was within the range of 0.3-50 ng mL^{-1} for cadmium. The correlation of determination (r^2) was 0.9966and the LOD was calculated based on three times of blank signal (six replicate blank measurements) divided by the slope of the calibration curve ($3S_b$/m) and it was 0.11 ng mL^{-1}.

3.5. Determination of Cd(II) ion in various real samples

In order to evaluate the performance of the synthetic $Fe_3O_4@SiO_2@Isa$ nano-composites, the suggested technique was used to determine Cd(II) in the real samples such as different water samples, under the optimum conditions. The recovery percentage relating to extract analyties from real samples were given in Table 1.

Table 1. Analysis of cadmium in different water

Sample	Analyte	Real sample (ng mL^{-1})	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)	RSD%
Tap (Tehran, Iran)	Cadmium	-	10.0	9.8	98.0	1.3
River water (Zayanderud, Isfahan. Iran)	Cadmium	2.4	10.0	12.2	98.0	1.6

4. CONCLUSION

In the current research for the first time, we introduce a novel magnetic nanosorbent consisted of SiO_2, Fe_3O_4 nanoparticles, and isatingroup and applied for rapid and facileseparation of trace quantities of cadmium(II) from various matrices. The characterization of this novel sorbent was performed using FT-IR, SEM, and XRD. Low LOD, and excellent yields with short extraction times are the main advantages of this magnetic nanocomposite. In conclusion, considering the obtained outcomes, the suggested new nanocomposite is facile, easy and fast and can be used in complex matrices.

REFERENCES
1. H. Zhang, D. Ma, Q. Xie, X. Chen, *Environ. Geol.* 38, 223 (**1999**).
2. S. Tangjuank, N. Insuk, J. Tontrakoon, V. Udeye, *Adsorption* 141, 10191 (**2009**).

3. M. Ghaemi, G. Absalan, *Microchim. Acta* 181, 45 (**2014**).

4. M. Faraji, Y. Yamini, M. Rezaee, *Talanta* 81, 831 (**2010**).

5. H. Bagheri, A. Afkhami, M. Saber-Tehrani, H. Khoshsafar, *Talanta* 97, 87 (**2012**).

6. B. Pan *et al.*, *Water Res.* 44, 815 (**2010**).

7. A. Tadjarodi, A. Abbaszadeh, M. Taghizadeh, N. Shekari, A. A. Asgharinezhad, *Mater. Sci. Engin: C* 49, 416 (**2015**).

8. M. Behbahani *et al.*, *Food chem.* 187, 82 (**2015**).

9. H. M. Marwani, M. U. Lodhi, S. B. Khan, A. M. Asiri, *J. Taiwan Ins. Chem. Eng.* 51, 34 (**2015**).

10. A. Bagheri *et al.*, *Microchim. Acta* 178, 261 (**2012**).

11. F. El Aroui *et al.*, *J. Taiwan Ins. Chem. Eng.* 45, 2725 (**2014**).

12. H. Sanaeepur, A. Kargari, B. Nasernejad, A. E. Amooghin, M. Omidkhah, *J. Taiwan Ins. Chem. Eng.* 60, 403 (**2016**).

13. M. Saraji, M. K. Boroujeni, *Anal. Bioanal. Chem.* 406, 2027 (**2014**).

14. S. Sadeghi, E. Aboobakri, *Microchim Acta* 178, 89 (**2012**).

15. H. Bagheri, A. A. Asgharinezhad, H. Ebrahimzadeh, *Food Anal. Methods* 9, 876 (**2016**).

16. S. S. Miri, M. Khoobi, F. Ashouri, F. Jafarpour, P. R. Ranjbar and A. Shafiee, *Turk. J. Chem.* 39, 1232 (**2015**).