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Extraction and preconcentration of Ni(II), Pb(II), and Cd(II) ions using a nanocomposite of the type Fe₃O₄@SiO₂@polypyrrole-polyaniline†

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In this study, the application of Fe₃O₄@SiO₂@polypyrrole-polyaniline magnetic nanocomposite was studied for Ni(II), Cd(II), and Pb(II) ions preconcentration extraction. In this regard, the silica layer prevents the Fe₃O₄ nanoparticles (NPs) from aggregating over a broad pH range value and simultaneously improves chemical stability and hydrophilicity. By using a Box–Behnken design, the effect of various parameters affecting the preconcentration was studied. FAAS was employed to quantify the eluted analytes. The detection limits are 0.09, 1.1, and 0.3 ng mL^{−1} for Ni(II), Cd(II) and Pb(II), ions, respectively. The relative standard deviations (RSDs%) were calculated for determining the method's precision, lower than 7.5%. The capacities of sorption are 75, 84, and 98 mg g^{−1}, respectively. With the usage of a certified reference material, the developed method was validated. After that, the validated method was employed to rapidly extract trace target ions from food samples and gave satisfactory results.

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1 Introduction

Heavy metals, which have been extensively utilized in diverse manufacturing processes such as combustion of fossil fuels, plating steel, metal forging, electronics, metallurgy, smelting, mining, electroplating, manufacturing of alkaline storage batteries, photographic materials, explosive manufacturing traffic, metal finishing, textiles, ceramics, printing, pigments, fuels and many others are unavoidably discharged into the environmental waters.^{1–3} These species can enter the human body *via* the food chain and endanger human health even at a low concentration.^{2,3} The biological molecules containing N, O, and S elements show a reasonable propensity for forming complexes to heavy metals.^{4,5} These interplays result in the breaking of hydrogen bonds, causing changes in the molecular structure of proteins and enzymes inhibition.⁴ The carcinogen and toxicity effects of heavy metal ions like those affecting the central nervous system (As(III), Hg(II) and Pb(II)); or skin, bones, or teeth (Ni(II), Cu(II), Cd(II), Cr(III)); the kidneys or liver (Hg(II), Pb(II), Cu(II), Cd(II));^{6–8} can be explained with these interactions.⁴

Consequently, monitoring and determining the proportion of heavy metal ions in food samples for an analytical chemist is necessary for identifying and monitoring toxicants in environmental samples. *Analytical chemists*. Identifying and monitoring

these toxicants in the mentioned samples. Therefore, developing a quick, simple, sensitive, green, and reliable method for monitoring heavy metals and determination is crucial.^{9–11}

Various preconcentration techniques such as ion exchange,¹³ chemical precipitation,¹⁴ liquid–liquid extraction,¹⁵ cloud point extraction,¹⁶ and solid-phase extraction (SPE) engineered for preconcentration of natural matrices, and heavy metal extraction,^{17–20} since the complexity of matrices, are mainly an issue, and proportion of the heavy metals in the actual samples is considerably low.¹²

SPE is the most widely employed extraction method for preconcentrating heavy metals from actual samples among the mentioned techniques. Simplicity, rapidity, cost-effectiveness, and low consumption of reagents are the main reasons for widespread SPE utilization.²¹ By the emergence of SPE, a wide range of sorbents like carbon nanotubes and graphene oxide,^{22–25} modified porous materials,^{26,27} and magnetic nanoparticles^{28–30} have been used.

In the past decades, utilizing nanostructured materials in analytical chemistry, specifically, the usage of Fe₃O₄ as a magnetic nanoparticle, attracted great attention since magnetic Fe₃O₄ nanoparticles (Fe₃O₄ NPs) not only has the nanometer-sized materials general features but also demonstrates magnetic property.^{31–33} In many cases, major environmental problems arose due to the difficulties of completely removing and separating sorbents from sample solutions.³⁴ Magnetic materials are capable of employing an external magnetic field; thus, they can simplify the solid sorbent's isolation from the sample solution and facilitate sample preparation procedures.³⁵ However, Fe₃O₄ nanoparticles which tend to oxidize, are not selective regarding complex matrices and

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prone to aggregate. Thus, surface functionalization of bare Fe_3O_4 NPS allows a reduction in aggregation and leads to higher selectivity. Another way to address this problem is core-shell nanostructures. The strong superparamagnetic properties of Fe_3O_4 NPs make them a perfect candidate for the synthesis of core-shell nanostructures in which these NPs act as the core. Among the various shells, due to the several unique characteristics of silica, it is an ideal selection: (a) silica shell can solve the aggregation problem of magnetite NPs in a broad pH range and reinforces their chemical stability, (b) silane coupling agents are able to modify the silica surface, and consequently, they can be modified by diverse chelators and (c) the layers of SiO_2 also have an excellent hydrophilicity behavior.^{36,37} From the theory of hard-soft-acid-base (HSAB), most heavy metal ions are soft acids, and they are capable of forming strong bonds with molecules/ions having S and N atoms which behave as a soft base.

The $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{polypyrrole-polyaniline}$ ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPy-PANI}$) magnetic nanocomposite is used in this work as a nano-sorbent for the purpose of preconcentration and rapid separation of $\text{Cd}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Pb}(\text{II})$ ions from numerous food samples. Characterization tests of sorbent were carried out with the Fourier transform infrared spectroscopy (FT-IR), elemental analysis, vibrating sample magnetometer (VSM), and transmission electron microscopy (TEM). Due to the superparamagnetic behavior of the nano sorbent, quick and straightforward separation of the solid materials is possible. Coating the magnetite NPs with PANI-PPy copolymer enhanced the selectivity and sorption capacity of the sorbents towards target analytes. Also, sorption capacity and surface area enhanced due to the nanosized property of sorbent. The optimum extraction conditions exploration was done with designing experiments approach with the help of the response surface methodology. In the final step, the extractive preconcentration and quantification of the target ions in diverse agricultural and sea food samples, conducted with the usage of the nano sorbent.

2 Experimental

2.1 Solutions and reagents

All analytical grade reagents including HCl, tetraethyl orthosilicate (TEOS), KCl, ammonium hydroxide (25%), FeCl_2 , HNO_3 , ammonium persulfate (APS), NaOH, FeCl_3 , aniline (Ani), pyrrole

(Py), (ethanol, methanol, and acetone) provided by the Merck company or Fluka and were utilized without any additional purification procedure. Stock solutions (1000 mg L^{-1}) of $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Ni}(\text{II})$ ions were acquired from Merck (Darmstadt, Germany). The distilled water used for the preparation of samples was double distilled water.

2.2 Instrumentation

All information about the instrumentation are mentioned in ESI.†

2.3 Solutions

In a microwave digestion chamber, the reference material was prepared by using 6 mL HCl (37% (w/w)) and 2 mL HNO_3 (65% (w/w)). Solutions were kept at room temperature, and the following program was accomplished: 2 min at 250 W, no radiation for 2 min, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W the venting process was done for 8 min.³⁸ Afterward, double distilled water was utilized for dilution of the residue.³⁸ 1000 mg L^{-1} solutions of K^+ , $\text{Al}(\text{III})$, $\text{Zn}(\text{II})$, $\text{Sn}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Fe}(\text{III})$, $\text{Hg}(\text{II})$, Na^+ , PO_4^{3-} , $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$, CrO_4^{2-} , $\text{Co}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Cr}(\text{III})$ were prepared in the solution of nitric acid 2% (v/v). The preparation of the working solution with double distilled water was done by stepwise dilution of the stock solution.

2.4 $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{polypyrrole-polyaniline}$ magnetic nanocomposite synthesis

2.4.1 $\text{Fe}_3\text{O}_4@\text{silica}$ synthesis. Previously we reported the NPs to synthesize procedure in which we used 25 mL 0.4 mol L^{-1} HCl solution to dissolve 5.2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.0 g of FeCl_2 .³⁵ In the next step, under N_2 atmosphere, the iron salts mixture was added into 250 mL of 1.5 mol L^{-1} sodium hydroxide dropwise and heated for 30 min at 80°C .³⁵ Afterward, the black precipitate was isolated by a strong magnet with the size of $15 \text{ cm} \times 12 \text{ cm} \times 5 \text{ cm}$ (1.4 Tesla). With the usage of distilled water and ethanol, the black precipitate was washed three times. As the next step, under vacuum conditions, magnetite NPs were dried for about six h. Then, in a 200 mL deionized water solution, 50 mL ethanol, 1.0 g of synthesized magnetite NPs and 3 mL NH_4OH (25%) were mixed. Afterward, under vigorous stirring, 2.5 mL of TEOS was added steadily to synthesize the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell NPs into the reaction mixture.³⁹ Using a permanent magnet, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs

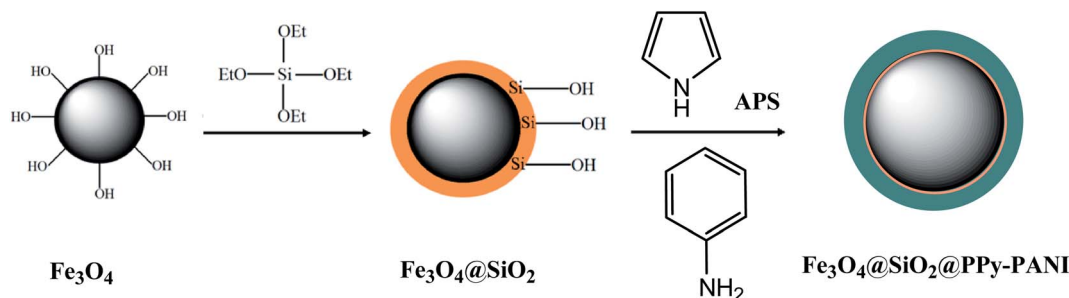


Fig. 1 A schematic diagram for the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPy-PANI}$ magnetic nanocomposite.



were isolated after 12 h stirring at 40 °C, then at room temperature, it was washed with ethanol and finally dried (Fig. 1).

2.4.2 Fe₃O₄@SiO₂ nanoparticles modification with copolymer. The Fe₃O₄@SiO₂ core-shell nanoparticles modifying procedure is given in two steps: At first, in 150 mL of HCl solution (1.0 mol L⁻¹), 1.0 g of Fe₃O₄@silica was dispersed and sonication was conducted for about 15 min. Then 1.0 mL Py and 1.3 mL Ani were added to the system and stirred for 30 min. Next, the temperature of the solution dropped to 0 °C as the next step, and in 1.0 mol L⁻¹ HCl solution, the stoichiometric concentration of APS was added dropwise. The polymerization process continued for about 12 h, and finally. As a result, a precipitate was required.⁴⁰ Subsequently, utilizing a strong magnet, the Fe₃O₄@SiO₂@PPy-PANI nano-material was isolated and washed with H₂O and CH₃OH continuously to ensure no possible unreacted reagents in the system and finally, at room temperature, they dried. A schematic diagram is illustrated in Fig. 1 for the Fe₃O₄@SiO₂@PPy-PANI nanocomposite synthesis.

2.5 Extraction process

In the batch mode, extraction of target ions was accomplished. By employing 50 mL 0.5 µg mL⁻¹ to mixture solutions, the sorption process was accomplished. Briefly, 1.0 mol L⁻¹ HCl and 1.0 mol L⁻¹ NH₃ were added dropwise to adjust the solutions' pH. After that, Fe₃O₄@SiO₂@PPy-PANI nanocomposite was added to the solutions. For complete extraction of the metal ions from the solution, it was agitated for a predetermined time.⁴¹ Based on concentration level change before and after the process with the help of FAAS, the absorbed amounts of the ions were calculated. The following equation determined sorption percentage:

$$\text{Sorption\%} = \frac{C_A - C_B}{C_A} \times 100$$

Each analyte's initial and final concentrations (mg L⁻¹) represented by C_A and C_B, respectively. The elution process was accomplished by preparing 5.4 mL of 1.7 mol L⁻¹ HNO₃ solution as the eluent. After that, with the help of the strong magnet, the sorbent was isolated from the solution. At the end, the metal ions clear solution was injected into FAAS to determine each ion's recovery.

2.6 Real sample pretreatment

The actual sample and certified reference materials pretreatment details are mentioned in ESI.†

3 Results and discussion

3.1 Material selection

Extraction recovery of the target ions is affected by the sorbent type. In this context, firstly, Fe₃O₄ NPs are covered with a silica layer to prevent aggregation of Fe₃O₄ NPs and improve their acid resistance. In this case, a protecting layer such as SiO₂ is needed since solutions of strong acids are used as eluent for

solid-phase extraction of metal ions, which may dissolve Fe₃O₄ NPs. Moreover, the surface of silica has the silanol moieties, which silane coupling agents can functionalize, and subsequently, various ligands can be immobilized on its surface. In the next step, Fe₃O₄@SiO₂ NPs are coated with a copolymer of aniline and pyrrole, which enhances the selectivity and sorption capacity of the nano-material towards the target species. Coordinating performance in the copolymer coating is enhanced due to its atoms being utilized as a proper functionalizing agent. With a simple and economical method, Fe₃O₄ can be synthesized in large quantities. Owing to the high surface area, these NPs have high sorption capacity. They are superparamagnetic, which means their separation from the extraction medium can be simply performed by employing a permanent magnet.⁵ Hence, the extraction ability of magnetite, Fe₃O₄@silica, Fe₃O₄@silica@PANI, Fe₃O₄@silica@PPy, and Fe₃O₄@silica@PANI-PPy sorbents was compared. The results indicated the efficiency of extraction. The Fe₃O₄@silica@PANI-PPy sorbent is higher than the others. The higher performance of Fe₃O₄@silica@PANI-PPy may be related to the possibility of chelate formation (more efficient interaction) with metal ions. Thus, it was considered as the best sorbent in this study.

3.2 Characterization

3.2.1 CHN analysis and FT-IR spectra. The KBr pellet method was utilized for recording the FT-IR spectra of Fe₃O₄@SiO₂@PANI-PPy nanocomposite. Owing to the coating of Fe₃O₄@SiO₂ NPs with PANI-PPy copolymer, the absorption peaks can be observed at 3403 cm⁻¹ (N-H), 1579 cm⁻¹ (C=N), and 1495 cm⁻¹ (C=C) additionally, CHN analysis exhibited the presence of 2.1% N in the structure of Fe₃O₄@SiO₂@PANI-PPy nanocomposite which proves the successful modification of NPs with PPy-PANI copolymer.

3.2.2 Transmission electron microscopy. TEM characterization technique was used (Fig. 2a) for studying the dimension of Fe₃O₄@SiO₂@PANI-PPy NPs and its surface morphology. Fig. 2a demonstrates a relatively thin layer of SiO₂ successfully coated Fe₃O₄ nanoparticles. Two recognizable regions with distinct electron densities can be observed in this figure which verifies that a core-shell structure is formed successfully.³⁶ The electron-dense region is related to average-sized magnetite cores around 15 nm (Fig. 1S†). The more translucent and less-dense region around the cores is the SiO₂ shell thickness of around 15 nm (Fig. 1S†).

3.2.3 Thermogravimetric analysis. The thermal analysis explored the thermal behavior and stability of the modified Fe₃O₄@SiO₂ NPS. Fig. 2b depicts the thermogravimetric (TG) plot of the nanocomposite. There were two thermal phenomena which the first one was related to the desorption of water molecules and took place up to 100 °C. From the TG curve also, it can be seen that the sorbent weight loss is around 10.2% when the sample is heated up to 500 °C, and subsequently, it is safe to say that the fabricated nano-material is stable. The weight loss of 6.6% in the range of 300–500 °C is related to the degradation of polymer layer. The results confirm that the



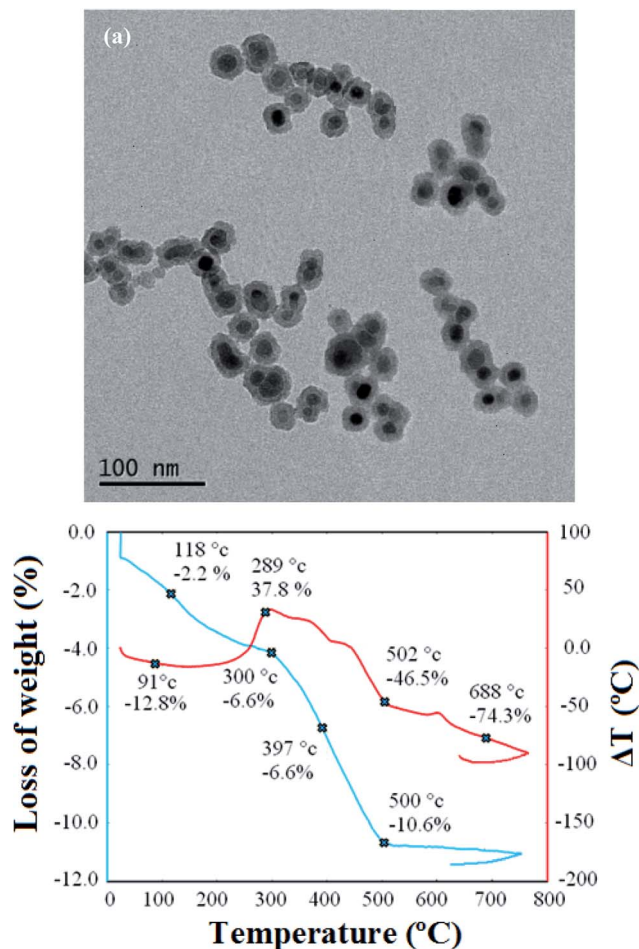


Fig. 2 (a) The TEM image and (b) the TG plot of the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPy-PANI}$ magnetic nanocomposite.

formation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ nanocomposite was performed successfully.⁴²

3.2.4 VSM and dynamic light scattering analyses. The sorbents must have superparamagnetic properties to separate under a magnetic field quickly. At room temperature, the magnetic properties of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, Fe_3O_4 , and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ with utilizing the magnetic property measurement were investigated, and the correlating curves can be seen in Fig. 3. As illustrated in this figure, the saturation magnetization of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ is 70, 40, and 26 emu g^{-1} , respectively, which is enough for MSPE process. It is known that the magnetization is zero when the external field approaches zero for superparamagnetic sorbent. In this work, the curve for hysteresis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ NPs passed through the zero point and exhibited superparamagnetic features.⁴³

The size of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ NPs also was explored by the DLS technique. The DLS size distribution of the sorbent is illustrated in Fig. 2S (ESI†). As depicted, the average diameter of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ NPs was about 35 nm with a relatively narrow distribution which demonstrates that there are no severe aggregates.

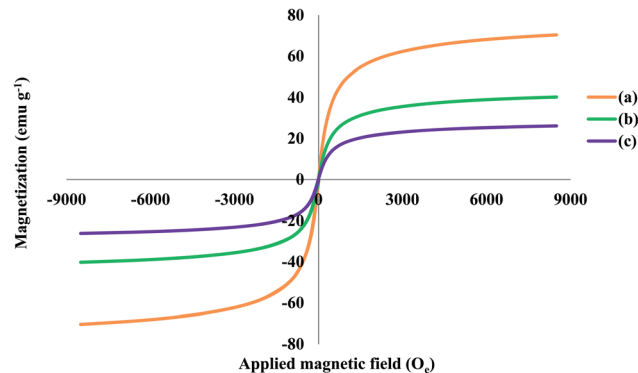


Fig. 3 Vibrating sample magnetometry plots of (a) Fe_3O_4 (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (c) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPy-PANI}$ NPs.

3.3 Method optimization

The parameters of (a) the eluent, (b) the sorption and (c) the elution step was optimized. In the ESI, the figures and data are represented (Fig. 3S and 4S, Table 1S†). The sorption time of samples are in the order of 9.0 min, and pH value is 6.2; application of 10 mg $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ NPs in the step of sorption, and the usage of a $1.7 \text{ mol L}^{-1} \text{HNO}_3$ as eluent with the volume of 5.4 mL; and finally for the elution time of 11.5 min had the best sorption and extraction recoveries.

3.4 Breakthrough volume

The preconcentration factor is affected in this regard, by spiking 1 mg Ni(II) , Pb(II) and Cd(II) ions in the range of 250–1750 mL solution, samples volume influence was studied thoroughly. After that, the SPE process was accomplished, and the results revealed that the recovery of the analytes remained quantitative (>95%) up to 1000 mL. Thereby, the simultaneous quantitative recovery of target ions on $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ nano sorbent can be obtained up to 1000 mL of sample volumes. Based on the sample and eluent volume, an enrichment factor of 185 is obtained that is desirable.

3.5 Interference assay

For the study of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ nano sorbent selectivity, the effect of various metal ions on the target ions extraction recovery was investigated. In Table 2S,† we summarized the tolerance of these potentially interfering ions (ESI,† ESM). From this information at pH 6.2, it is safe to say that high concentrations of potentially interfering species indicated no significant effect on the recovery of the analytes. Thereby, the developed extraction method can be employed for the determination of the target analytes in complicated samples reasonably.

3.6 Sorption capacity study

$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PANI-PPy}$ nano sorbent's sorption capacity (AC) was studied by using a known concentration of each ion. After sorption, the equilibrium amounts of the target metals were



Table 1 Determination of Cd(II), Pb(II) and Ni(II) in sea food mix certified reference material

Concentration (mg kg ⁻¹)			Relative error (%)
Element	Certified	Found	
Cd	4.764	4.63	-2.8
Pb	2.779	2.68	-3.6
Ni	3.071	2.90	-5.6

established by FAAS. Accordingly the maximum AC of the new nano-material for Pb(II), Ni(II), and Cd(II) ions, was 84, 98, and 75 mg g⁻¹, respectively.

3.7 Analytical features and method validation

Under the optimum conditions, calibration plots were attained to determine target ions. The linear range was 0.3–100 ng mL⁻¹ for Cd(II), 3–150 ng mL⁻¹ for Pb(II), and 1–130 ng mL⁻¹ for Ni(II). The determination correlation (r^2) was around 0.994 for Pb(II), 0.995 for Cd(II) and 0.996 for Ni(II) ions. Based on $LOD = 3S_b/m$, the detection limits were calculated. Ten replicate blank signals of the standard deviation, represented by S_b and calibration plot slope is m after the extraction process. When samples volume was 1000 mL, LOD calculated for Pb(II) about 1.1 ng mL⁻¹ and for Ni(II) ions and Cd(II) is around 0.3 ng mL⁻¹ and 0.09 ng mL⁻¹, respectively. The

repeatability of proposed MSPE method was evaluated in the 30 ng mL⁻¹ of Ni(II), Pb(II), and Cd(II) ions ($n = 3$) standard solution and the relative standard deviations (RSDs%) are 6.8, 5.4 and 7.5% respectively.

To determine the reliability of the new method, the 02-2932 CRM seafood mix used, under the optimal conditions, target ions were determined in this sample. A reasonable correlation was observed between the actual value of the mentioned ions in CRM (Table 1) and the obtained value by the developed method. Thereby, the present method can be employed as an accurate and reliable procedure for the preconcentration and determination of target analytes in actual samples.

Besides, the performance of the developed extraction method is compared with other methods (ESI†). The comparison exhibited that the present method has suitable LODs, enrichment factors, and sorption capacities compared to the former works. The compared features of the developed method are similar or, in some cases are, act superior to the other methods. Thus, this method is acceptable in terms of analytical efficiency.

3.8 Analytical application to the real sample

To reduce the undesirable matrix influence in the case of accurate sample analysis, the developed extraction method was applied for the extraction of target analytes at pH 6.2. Table 2 summarizes the relative recovery of these ions in various samples, which are almost quantitative in all cases.

Table 2 Determination of Cd(II), Pb(II) and Ni(II) ions in sea food and agricultural samples

Sample	Element	Real sample (ng g ⁻¹)	Added (ng g ⁻¹)	Found (ng g ⁻¹)	Recovery (%)	RSD (%)
Fish 1 (Persian Gulf)	Cd	6.7	10.0	15.6	89.0	6.8
	Pb	15.1	10.0	24.7	96.0	5.0
	Ni	21.3	10.0	30.5	92.0	4.9
Fish 2 (Persian Gulf)	Cd	8.0	10.0	17.0	90.0	7.3
	Pb	29.8	10.0	38.5	88.0	6.4
	Ni	55.3	10.0	64.0	87.0	7.9
Shrimp	Cd	23.5	10.0	32.1	86.0	3.9
	Pb	25.0	10.0	36.9	119	6.5
	Ni	33.4	10.0	42.2	88.0	7.8
Canned tuna	Cd	5.1	10.0	14.6	95.0	6.0
	Pb	75.4	10.0	84.9	95.0	8.5
	Ni	40.1	10.0	48.5	84.0	5.2
Fish (Caspian Sea)	Cd	19.6	10.0	29.0	94.0	4.6
	Pb	60.5	10.0	71.6	111	5.9
	Ni	98.4	10.0	107	86.0	6.1
Fish (Siahroud River)	Cd	32.2	10.0	41.5	93.0	5.9
	Pb	100	10.0	109	90.0	9.4
	Ni	25.3	10.0	36.0	107	8.3
Broccoli	Cd	3.2	10.0	13.5	103	7.1
	Pb	8.9	10.0	17.8	89.0	7.4
	Ni	6.3	10.0	15.9	96.0	6.5
Lettuce	Cd	3.3	10.0	12.9	96.0	6.9
	Pb	12.6	10.0	23.0	104	5.0
	Ni	10.0	10.0	18.9	89.0	6.7
Mushroom	Cd	2.3	10.0	12.2	99.0	8.5
	Pb	5.5	10.0	15.6	101	4.1
	Ni	9.7	10.0	18.7	90.0	6.6



4 Conclusion

Based on the application of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPy-PANI}$ nano sorbent in magnetic solid-phase, a reproducible, rapid, selective and straightforward extraction method for Ni(II) , Pb(II) , and Cd(II) ions determination was developed. Compared to the traditional adsorbents, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPy-PANI}$ nano sorbent exhibited several advantages, such as high sorption capacities, low detection limits, and high preconcentration factors. Also, besides the nanostructure characteristics, the nano sorbent showed magnetically-assisted separation, which leads to obtaining satisfactory results employing lower amounts of the nano-sorbent and solvent, and the method is not time-consuming.

Conflicts of interest

The authors declare that they have no conflict of interest.

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