A fungal functionalized magnetized solid phase extractor for preconcentrations of Pb(II), Mn(II), and Co(II) from real samples

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A B S T R A C T

Due to increasing industrialization and overpopulation, the amount of toxic metals is increasing in the environment, including air, soil, water, and food. Solid phase extraction is an efficient and ideal technique to preconcentrate the toxic metals before their measurements by analytical instruments. *Russula brevipes* was immobilized on γ-Fe$_2$O$_3$ magnetic nanoparticles and employed as a SPE sorbent to preconcentrate the trace level of Pb(II), Mn(II), and Co(II). To investigate the extraction conditions, significant experimental parameters were examined in details. LODs were calculated as 0.022, 0.015, and 0.024 ng mL^{-1} for Pb(II), Mn(II), and Co(II), respectively. The biosorption capacities of *R. brevipes* immobilized γ-Fe$_2$O$_3$ were calculated as 43.1 mg g^{-1} for Pb(II), 54.9 mg g^{-1} for Mn(II), and 49.7 mg g^{-1} for Co(II). Pb(II), Mn(II), and Co(II) in food samples at trace levels were preconcentrated by applying the developed method.

1. Introduction

Heavy metals, which are well known pollutants, can have a variety of negative impacts on the environment and organisms even at trace levels. While these elements are present in our environment at low levels and necessary for humans even at trace levels, excessive concentrations of them can potentially be hazardous in both the short- and long term (Ali, Khan, & Ilahi, 2019; Sulejmanović et al., 2022). For these reasons, one of the most significant areas of analytical chemistry is determination of metal element concentrations in environmental sources (Tavallali et al., 2019). Numerous practical spectroscopic methods, including inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma optical emission spectrometer (ICP-OES), can be used to measure the trace concentrations of metal ions in various matrices (Naeemullah et al., 2016). Because of the matrix's interfering effects, direct instrumental determination of toxic metals at trace quantities (in µg/L and or µg/kg) can have reduced precision and sensitivity although there are different analytical tools available for correction. To solve this limitation, preconcentration and matrix elimination methods such as solid phase

extraction (SPE) (Solangi, Memon, & Bhanger, 2009; Karadaş & Kara, 2013), solvent extraction (Farajzadeh, Bahram, Zorita, & Mehr, 2009), coprecipitation (Atanassova, Stefanova, & Russeva, 1998), and ion exchange (Kuroda, Hayashibe, Oguma, & Kurosu, 1989) have been frequently employed before their instrumental measurements.

SPE is an attractive technique because of its advantages such as ease of application, low cost, and not requiring the use of potentially harmful organic solvents. This technique also provides a high preconcentration factor and a lower extraction time (Nabid et al., 2012; Behbahani et al., 2014). Biosorbents, which are sorbents of biological origin, are of particular interest due to their rapid absorption and reversible desorption of metal ions. (Das, Vimala, & Karthika, 2008). The methods based on the use of biosorbent have also advantages over conventional technologies due to their low cost, great efficiency, and production of no waste throughout the procedure (Yalçın, Özdemir, & Kılınç, 2018). In addition to these features, biomass is preferred by researchers to align with the concept of sustainable development (Zhou et al., 2019). The bioaccumulation of metals by biological materials such as fungi, algae, agricultural and bacterial biomass containing functional groups such as amino, hydroxyl and carboxyl results from the binding of these groups to metals through adsorption, complexation and ion exchange mechanisms

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(Mohammed, Kapri, & Goel, 2011). However, the studies showed that immobilization of biosorbent to support material improves its analytical performance and re-usability. Iron-based nanoparticles as support material are economical and have low toxicity to organisms (Zhu et al., 2019). Because of their distinctive qualities, they have been thoroughly researched as excellent remediation materials (Fajardo et al., 2015; Kajani & Bordbar, 2019). Due to their magnetic properties, they are preferred because they can be easily separated from the reaction medium by an external magnetic field (Safarikova & Safarik, 1999).

Analysis of toxic metals in environmental sources and food samples at trace levels requires highly sensitive analytical instruments such as ICP-OES (Sneddon, Richert, & Hardaway, 2019; Lee, Park, & Lee, 2023). The inductively coupled plasma enables the generation of excited atoms and ions that produce electromagnetic radiation with a certain element's characteristic wavelengths. ICP-OES is currently more used for elemental analysis because ICP-MS devices are significantly more expensive (Shishov, Gerasimov, & Bulatov, 2022). Consequently, the ICP-OES was selected for this study.

In this study, Pb(II), Mn(II), and Co(II) in various water, beverages, and food samples were preconcentrated by applying the SPE method and then measured by ICP-OES. *Russula brevipes* is not popular in some regions due to its low flavor. The hard and quick worming of the fleshy part is effective in this. The fungus grows in low humidity forests, oak groves, under coniferous trees and in groups and emerges in spring. Although the medical effects of studies on macrofungi have increased considerably in the world, there are very few studies on the environmental biotechnology effects of macrofungi, especially for heavy metal preconcentration studies. There is a need for scientific attention to this issue in the world. Therefore, in this study, *R. brevipes* was used as biomass to determine some heavy metals such as Pb(II), Mn(II), and Co (II) in real samples by using the SPE method. For this, *R. brevipes* was immobilized on γ-Fe$_2$O$_3$ magnetic nanoparticles for use as a solid phase bio-extractor and then characterization studies were carried out. In addition, the accuracy and reliability of the proposed method have been demonstrated by using certified reference materials.

2. Material and methods

2.1. Reagents and solutions

Ultra-pure water (18.2 MΩ cm) was obtained from Milli-Q Millipore. Analytical purity chemicals were used in the experiments and all solutions were prepared using ultra-pure water. Pb(II), Mn(II), and Co(II) stock solutions at 1000 mg L^{-1} (Merck, Darmstadt, Germany) were diluted to desired concentration by ultra-pure water. NIST 1643e, EU-L-2 (EnviroMAT Waste Water), NWTM-15 spiked/fortified water (LGC,), NCS ZC 73350 (National Analysis Center for Iron and Steel, China), and NCS ZC 73014 (National Analysis Center for Iron and Steel, China) were already available in lab. All of the lab's glasswares were cleaned with HNO$_3$ prior to usage. All of the experiments were applied three times.

2.2. Instrumentation

A Perkin Elmer, Optima 2100 DV, inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to measure the concentrations of Pb(II), Mn(II), and Co(II). Filtering columns (1.0 cm × 10.0 cm) with polypropylene frites were used in SPE experiments. The flow rate of solutions was adjusted by using a peristaltic pump (Waters Marlow model 323-Milford, MA, USA).

2.3. Immobilization of Russula brevipes to γ-Fe₂O₃ nanoparticles

R. brevipes was used as biomaterial and it was collected from Arslanköy, Mersin, (Turkey). It was carefully washed with purified water to remove contaminants and dried at room temperature. The dried fungus was broken up and processed into a powder by using laboratory

blender. The powdered biomaterial was kept in an oven at 80 °C for one day to terminate its vital functions.

γ-Fe$_2$O$_3$ nanoparticles were synthesized by a method given in literature. FeCl$_3$ and FeCl$_2$ (mole ratio 2:1) were dissolved in 40 mL of distilled water and 30 mL of NH$_3$ was added to it drop-wise for a time of 60 min at 80 °C by vigorously stirring. The resulting black solution was filtered and γ-Fe$_2$O$_3$ as black precipitate was washed with distilled water until it was neutral. Then, it was dried in an oven at 90 °C for a day (Kılınç, 2016). The immobilization procedure of *R. brevipes* on the γ-Fe$_2$O$_3$ nanoparticles could be summarized as follows: 0.2 g of dried *R. brevipes* powder was added to 10 mL of suspension containing 0.8 g of γ-Fe$_2$O$_3$ nanoparticles and then thoroughly mixed. This suspension was refluxed at 65 °C for 60 min. After this procedure, the paste was heated in an oven at 100 °C for 2 h to obtain the dry mixture.

2.4. Preconcentration procedure

The pH of 100 mL of 20 ng mL^{-1} of Pb(II), Mn(II), and Co(II) solution was adjusted by adding required amounts of diluted HCl and NaOH. It was passed through the *R. brevipes* immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles packed SPE column by using a peristaltic pump. Then, 5.0 mL of 1.0 mol/L acid solution was passed through the column to elute the retained Pb(II), Mn(II), and Co(II) ions before their measurements by ICP-OES.

The applicability of the developed method was tested by applying to real samples that were bought from local markets. The solid samples were digested in an analytical microwave oven before the SPE procedure. For completing the digestion step, the samples were added to a 5.0 mL mixture of HNO$_3$:HCl:H$_2$O$_2$ (1:1:0.2) then transferred to a microwave oven at 170 °C and kept for 5 min. Then the temperature reached 200 °C within 15 min and held for 1.0 min at this temperature. The temperature was then lowered to 100 °C and held for 20 min. Before the liquid samples were applied to SPE, they were diluted to the desired volume. Certified water samples were applied directly to the procedure that we developed after pH adjustment.

3. Results and discussion

3.1. Surface chemistry of biosorbent

FT-IR spectra were recorded to observe the incorporation of *R. brevipes* immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles with and without Pb(II), Mn(II), and Co(II) and also FT-IR analyses are shown in Fig. 1. The peaks at 1056, 1254, and 2990 cm^{-1} could ascribe to the C—O stretching, C—N stretching of amine and C—H stretching of the aromatic ring of fungal surface, respectively. Significant differences were observed in the FT-IR spectra after metal ion binding on the biosorbent surface, this trend can be attributed to the complexation of Pb (II), Mn(II), and Co(II) with the surface functionalities of *R. brevipes*.

According to the hard and soft acids and bases theory, Pb(II) and Co (II) are classified as borderline acids while Mn(II) is hard. From this perspective, it could be concluded that the *R. brevipes* could include functional groups such as amine, alcohol, ester, acetate, carbonate, nitrate, phosphate, phenylamine, sulphate derivates (Ozdemir, Okumus, Dundar, & Kilinc, 2013). When theoretical approaches are evaluated together with FTIR results, it could be concluded that the mechanism of adsorption could be based on the complexation of Pb(II), Mn(II), and Co (II) with amine rich functional groups.

It could be concluded from SEM and EDX investigations (Fig. 2) that *R. brevipes* immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles gave a heterogeneous surface and Pb(II), Mn(II), and Co(II) bound to this surface. *R. brevipes* is a natural component of biological origin and it is an expected result to give a heterogeneous surface after being immobilized to the surface of the γ-Fe$_2$O$_3$. As seen in Fig. 2a, and b there is no peak due to Pb(II), Mn(II), and Co(II) were detected. Fig. 2c, d, and e shows the surface microimages of *R. brevipes* immobilized γ-Fe$_2$O$_3$ magnetic
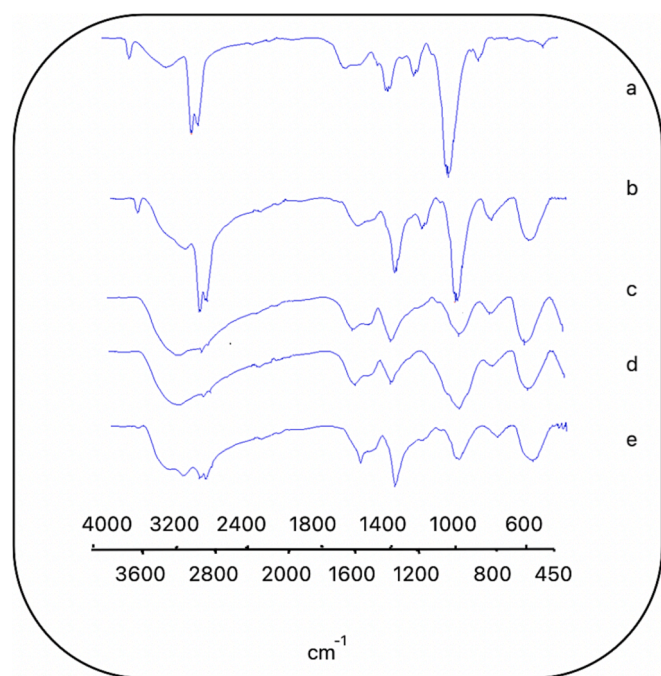
Fig. 1. FT-IR spectra of a. *R. brevipes*, b. *R. brevipes* immobilized γ-Fe₂O₃ magnetic nanoparticles, c. Pb(II), d. Mn(II) and e. Co(II) loaded *R. brevipes* immobilized γ-Fe₂O₃ magnetic nanoparticles.

nanoparticles after adsorption of Pb(II), Mn(II), and Co(II). From EDX results, it is clearly concluded that the adsorbed metal ions were detected on the sorbent surface. The percentages of targeted metal ions were not given due to the fact that the heterogeneous of surface. It was evaluated that the result of chemical analysis at any point where the EDX spectrum was taken would not be compatible with other points.

3.2. Optimization of the method

Important experimental parameters such as the pH value of the solution, sample flow rate, the effect of amounts *R. brevipes* and γ-Fe₂O₃ magnetic nanoparticles, the effect of eluent solution, and the effect of the sample volume were investigated in details to achieve maximum preconcentration yield.

Pb(II), Mn(II), and Co(II) target ions were simultaneously preconcentrated from aqueous solutions with pH values ranging from 2.0 to 9.0 (flow rate: 1.0 mL min⁻¹). Obtained results are presented in Fig. S1. It could be concluded from the results that, sorption performances for targeted ions were weak at pH < 5. This phenomenon could be explained by the fact that competition between Pb(II), Mn(II), Co(II), and H₃O⁺ ions. The best pH value was found to be 5.0 and 6.0 for all ions. Above pH 7.0, recovery begins to decrease slightly under basic conditions. Metal cations develop hydroxide complexes as a result of the alkaline environment. It is hypothesized that the biosorption efficiency of *R. brevipes* immobilized γ- Fe₂O₃ magnetic nanoparticles decreased due to the increasing of metal hydroxide precipitates at high pH values. The optimum pH was identified as pH 6.0 based on simultaneous determination and quantitative recovery results for Pb(II), Mn(II), and Co(II) when using *R. brevipes* immobilized γ- Fe₂O₃ magnetic nanoparticles as a biosorbent.

The equilibrium between the analyte ions and the biosorbent is affected by a number of factors, including the sample flow rate. The flow rate of the sample solution affects the quantitative recovery and desorption of analytes on the adsorbent in SPE operations. The effect of the sample solution flow rate on the recovery of Pb(II), Mn(II), and Co (II) from *R. brevipes* immobilized γ- Fe₂O₃ magnetic nanoparticles was evaluated at the optimum pH value and also metal solutions was passed

through the SPE column between the flow rate of 1.0–6.0 mL min⁻¹. The results are depicted in Fig. S2. Quantitative recoveries of Pb(II), Mn(II), and Co(II) were obtained as 95.9 %, 96.4 %, and 98.7 %, respectively at a 3.0 mL min⁻¹ flow rate. As the flow rate increased from 3.0 to 6 mL min⁻¹, quantitative recoveries of Pb(II), Mn(II), and Co(II) were decreased from 95.9 % to 58.4 %, from 96.4 % to 60.1 %, and from 98.7 % to 61.5 %, respectively. This is due to insufficient contact time between the biosorbent and the analyte ions. So, 3.0 mL min⁻¹ was selected as the best flow rate.

Varying masses of *R. brevipes* of 50, 75, 100, 150, 200, and 250 mg were tested to determine the best quantitative recovery at pH:6.0 and flow rate of 3.0 mL min⁻¹. The results are given in Fig. S3a Quantitative recoveries percentage raised from 86.3 % to 98.7 %, from 89.1 % to 96.2 % and from 88.4 % to 99.1 % for Pb(II), Mn(II), and Co(II) respectively, when the amount of *R. brevipes* rised from 75 mg to 100 mg. Increasing the amount of *R. brevipes* means more surface area and binding sites, so an increase in recoveries is a natural result. It was decided that 100 mg of *R. brevipes* was the ideal biosorbent amount for the following experiments. Additionally, the quantity of γ- Fe₂O₃ magnetic nanoparticles utilized as support material at varied masses of 50, 75, 100, 150, 200, and 250 mg was examined for quantitive revovery of tested metal ions at pH:6.0 and flow rate 3.0 mL min⁻¹. According to Fig. S3b, 100 mg of γ-Fe₂O₃ magnetic nanoparticles were the most ideal amount of support materials and the quantitative recoveries of Pb(II), Mn(II), and Co(II) were calculated as 95.3 %, 97.8 %, and 96.1 %, respectively.

Table 1 shows the obtained results after applying HCl and HNO₃ at different concentrations (0.5 and 1.0 mol/L) and volumes (3 and 5 mL) as desorption eluents at optimum experimental conditions. The desorption eluent should have both the lowest concentration to avoid damaging the sorbent surface and the lowest possible volume required for a high enrichment factor. Considering these factors, the recovery values of Pb(II), Mn(II), and Co(II) were found as 100 ± 1.2 %, 100.9 ± 1.2 %, and 100.3 ± 1.1 %, respectively when using 5 mL of 1 mol/L HCl.

The concentration of metal ions is known at trace levels in real samples such as biological, food, and environmental samples. After the digestion of samples, the dilution volume of sample solution should be considered in SPE experiments to obtain high preconcentration factor. From this perspective, the volume of sample solution is a critical parameter that should be optimized during the SPE procedure. Under the best experimental circumstances, a solution of 25, 50, 100, 200, 250, 300, 350, 400, and 500 mL volumes of Pb(II), Mn(II), and Co(II) were applied to the SPE column in order to establish the appropriate sample volume for this suggested method. As seen in Fig. S4, when 500 mL sample volume was used, Pb(II), Mn(II), and Co(II) ions were recovered quantitatively at the rates of 95.4 %, 96.3 %, and 96.9 %, respectively. By considering the 500 mL of sample volume and 5 mL of final elution volume, the theoretical enrichment/preconcentration factor could be calculated as 100 for tested metal ions.

3.3. Effect of interference cations

Analytical techniques used to determine the analyte concentration may have been interfered with by coexisting ions from the matrix. Mono- (K(I), Na(I)), di- (Ca(II), Mg(II), Fe(II), Cd(II), Zn(II), Hg(II) and trivalent (Al(III)) cations were analyzed as possible interfering ions. Individually, these ions were added to a solution that already included 100 ng/L of Pb(II), Mn(II), and Co(II). The results of the study are depicted in Table 2. It is clearly seen that interfering cations did not interfere with the recovery and determination of the target ions.

3.4. Loading and elution cycles

The re-usability of the extraction column in SPE studies is very important in terms of the economy of the proposed method. A SPE column package with *R. brevipes* immobilized γ-Fe₂O₃ magnetic
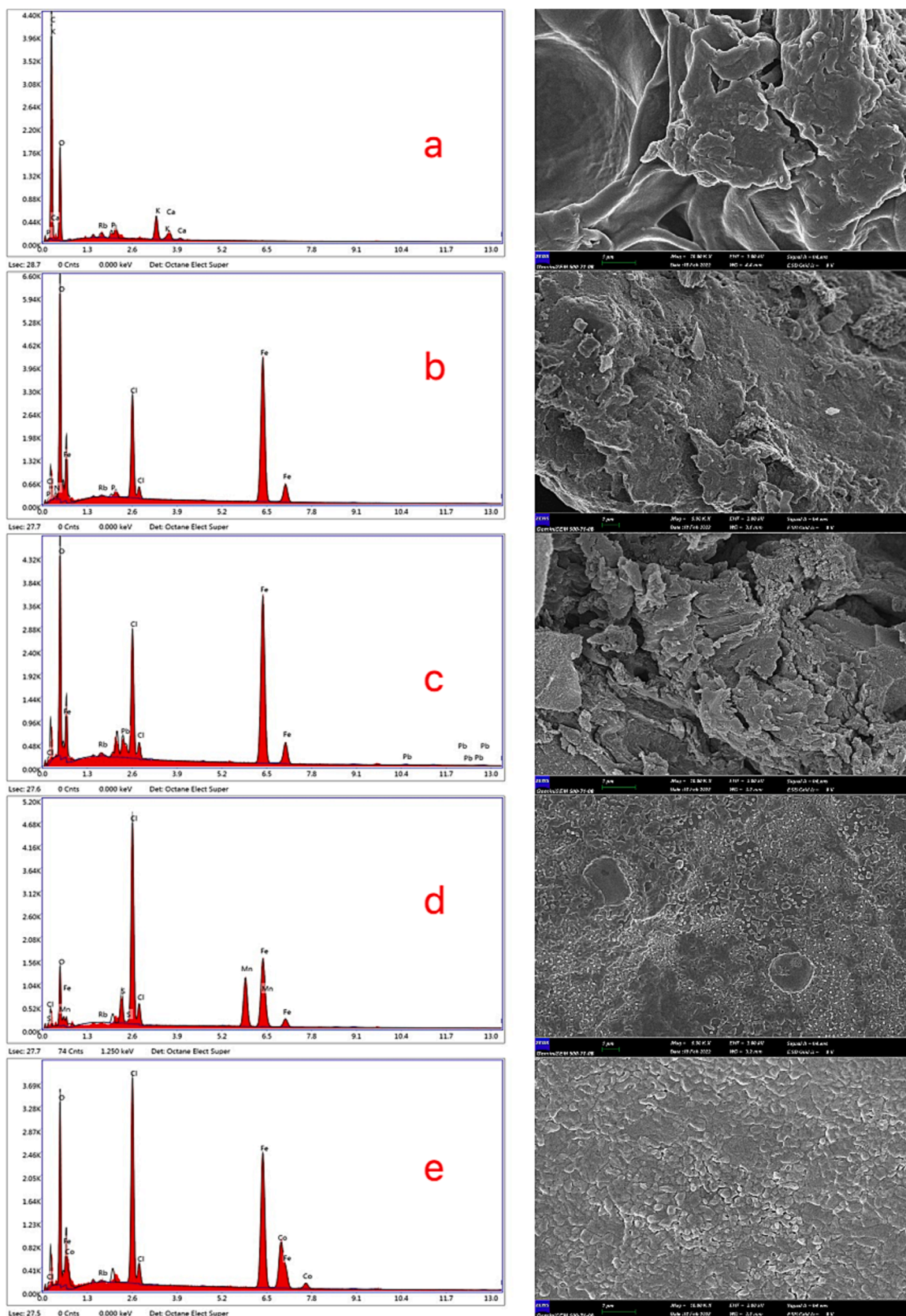
Fig. 2. EDX spectra and morphological characterization through SEM images a. *R. brevipes*, b. *R. brevipes* immobilized γ-Fe₂O₃ magnetic nanoparticles, c. Pb(II), d. Mn(II) and e. Co(II) loaded *R. brevipes* immobilized γ-Fe₂O₃ magnetic nanoparticles.

Table 1
Eluent type volume and concentration.

Eluent Type	Volume (mL)	Conc., (mol/L)	Recovery (%)		
			Pb(II)	Mn(II)	Co(II)
HCl	3	0.5	85.8 ± 0.8	90.6 ± 1.4	92.1 ± 1.3
	5	0.5	95.1 ± 1.6	96.1 ± 1.6	97.5 ± 1.4
	3	1	96.2 ± 1.3	97.1 ± 1.3	96.8 ± 1.5
	5	1	100 ± 1.2	100.9 ± 1.2	100.6 ± 1.1
HNO₃	3	0.5	82.7 ± 0.9	90.8 ± 1.8	90.1 ± 1.6
	5	0.5	93.2 ± 1.4	93.9 ± 1.1	94.3 ± 1.7
	3	1	94.9 ± 0.9	93.9 ± 1.5	95.8 ± 1.2
	5	1	96.3 ± 1.5	97.6 ± 0.9	99.7 ± 1.8

Table 2
Effect of interference studies on recovery of Pb(II), Mn(II), and Co(II).

Interferences	Interference to metal ion ratio	Recovery (%)		
		Pb(II)	Mn(II)	Co(II)
Na(I)	5,000	96.9 ± 1.4	97.3 ± 1.1	98.9 ± 1.6
K(I)	5,000	95.3 ± 1.1	97.4 ± 1.4	98.5 ± 1.3
Ca(II)	100	98.1 ± 1.6	98.1 ± 0.8	99.1 ± 1.5
Mg(II)	100	98.9 ± 1.8	97.9 ± 1.5	98.3 ± 1.4
Fe(II)	10	98.6 ± 0.9	97.6 ± 1.3	98.4 ± 1.7
Cd(II)	5	96.4 ± 1.1	95.8 ± 0.9	95.6 ± 1.2
Zn(II)	5	97.5 ± 1.2	96.9 ± 1.5	95.2 ± 1.6
Hg(II)	5	96.2 ± 1.4	96.8 ± 1.4	95.9 ± 1.4
Al(III)	5	95.3 ± 1.3	96.1 ± 1.8	96.3 ± 1.5

nanoparticles were efficiently employed to absorb Pb(II), Mn(II), and Co(II) over the course of 30 cycles of loading and elution step to check for reusability. As seen in Fig. S5, at the end of 30 cycles, target ions were still quantitatively recovered.

3.5. Analytical performance and biosorbent capacity

Under the best circumstances determined as mentioned above, the limits of detection (LOD) and limits of quantification (LOQ) after preconcentration were determined as 0.022 ng mL^{-1} for Pb(II), 0.015 for Mn(II) ng mL^{-1}, and 0.024 ng mL^{-1} for Co(II) and 0.074 ng mL^{-1} for Pb (II), 0.051 ng mL^{-1} for Mn(II), and 0.080 ng mL^{-1} for Co(II), respectively. LOD and LOQ are defined as LOD = 3Sb/m and LOQ = 10Sb/m where Sb is the standard deviation (SD) of ten replicate blank signals; and m is the slope of the calibration curve after preconcentration. Linear calibration graphs with correlation coefficients (R^2) were Pb(II) (0.9999), Mn(II) (0.9987), Co(II) (0.9990). The linear range was obtained as 0.025–20 for all target ions. The relative standard deviation (RSD) was calculated as 2.9 % Pb(II), 2.0 % Mn(II), and 3.1 % Co(II). These RSD values demonstrated that the suggested technique has good precision for identifying these metals in sample solutions.

The biosorption capacity is expressed as the greatest metal amount that can be absorbed in 1 g of biosorbent (mg g^{-1}). The biosorption capacity of *R. brevipes* immobilized γ- Fe₂O₃ magnetic nanoparticles was

43.1 mg g^{-1} for Pb(II), 54.9 mg g^{-1} for Mn(II), and 49.7 mg g^{-1} for Co (II).

3.6. The method validation and applicability

Certified reference materials (CRM) were used to validate the suggested extraction technique. The following CRMs were utilized for this aim: NIST 1643e (Trace Elements in Water), EU-L-2 (Waste Water), NWTM-15 (Fortified water - Trace elements), NCSDC 73350 (Leaves of poplar), and NCSZC 73014 (Trace Elements in Tea). It would be conceivable to state that the accuracy of the suggested procedure has been verified in light of the satisfactory results acquired. The technique was then successfully applied to tap water, beer, energy drink, Turkish coffee, ready-to-use coffee, sugar, salt, honey, milk, cheese, rice, some fruits, and vegetable samples. The results can be seen in Table 3.

Table 4 includes a comparison of the proposed separation-preconcentration approach for water, various beverages, and food samples with certain methods in the literature. The detection limits of the procedure are good for ICP-OES determinations of Pb(II), Mn(II), and Co(II) trace ions.

4. Conclusion

An alternative biosorbent based SPE column was prepared by using *R. brevipes* immobilized with γ-Fe₂O₃ magnetic nanoparticles and performed to develop for preconcentration of Pb(II), Mn(II), and Co(II). Several experimental parameters were investigated in detail to find the

Table 3
Applicability of the method to CRMs and real samples.

Sample	Pb(II)	Mn(II)	Co(II)
NIST 1643e, certified, ng mL^{-1}	19.63 ± 0.21	38.97 ± 0.45	27.06 ± 0.32
NIST 1643e, found, ng mL^{-1}	19.34 ± 0.34	38.74 ± 0.92	26.89 ± 0.78
EU-L-2, certified, ng mL^{-1}	41	120	81
EU-L-2, found, ng mL^{-1}	41 ± 2	119 ± 5	81 ± 0.5
NWTM-15, certified, ng mL^{-1}	11.8	18.4	15.1
NWTM-15, found, ng mL^{-1}	11.6 ± 0.5	18.2 ± 0.5	15.0 ± 0.7
NCS ZC73350, certified, μg g^{-1}	1.5 ± 0.3	45 ± 4	0.42 ± 0.03
NCS ZC73350, found, μg g^{-1}	1.5 ± 0.08	45 ± 1.7	0.41 ± 0.02
NCS ZC73014, certified, μg g^{-1}	1.5 ± 0.2	500 ± 20	0.22 ± 0.02
NCS ZC73014, found, μg g^{-1}	1.5 ± 0.09	491 ± 32	0.22 ± 0.01
Tap water 1, ng mL^{-1}	<LOD	14.5 ± 1.1	4.5 ± 0.1
Tap water 2, ng mL^{-1}	<LOD	20.2 ± 1.3	5.1 ± 0.1
Beer, ng mL^{-1}	<LOD	33.6 ± 2.0	12.3 ± 0.8
Energy drink, ng mL^{-1}	<LOD	106 ± 4	24.0 ± 1.5
Turkish coffee, ng/g	<LOD	1.0 ± 0.05*	8.0 ± 0.4*
Ready to use coffee, ng/g	<LOD	1.5 ± 0.04*	1.1 ± 0.03*
Sugar, ng/g	<LOD	5.9 ± 0.3*	3.4 ± 0.1*
Salt, ng/g	10.2 ± 0.3	1.3 ± 0.06*	2.0 ± 0.1*
Honey, ng/g	<LOD	3.2 ± 0.1*	0.9 ± 0.02*
Strawberry jar, ng/g	<LOD	7.0 ± 0.4*	2.0 ± 0.1*
Milk, ng/g	<LOD	3.4 ± 0.1*	1.1 ± 0.04*
Rice, ng/g	5.4 ± 0.1	15.4 ± 0.9*	10.1 ± 0.3*
Red lentil, ng/g	12.2 ± 0.4	24.1 ± 1.1*	12.3 ± 0.3*
Kidney bean, ng g^{-1}	<LOD	9.8 ± 0.4*	7.0 ± 0.2*
Bean, ng/g	<LOD	35.1±*	15.3 ± 0.4*
Baby biscuit, ng/g	<LOD	10.1 ± 0.7*	5.6 ± 0.1*
Cheese, ng/g	<LOD	1.5 ± 0.05*	5.0 ± 0.1*
Olive, ng/g	<LOD	12.1 ± 1.0*	3.4 ± 0.09*
Onion, ng/g	10.2 ± 0.3	20.0 ± 1.1*	4.0 ± 0.09*
Walnut, ng/g	<LOD	8.3 ± 0.3*	3.0 ± 0.1*
Hazelnut, ng/g	<LOD	11.1 ± 0.4*	5.1 ± 0.2*
Peanut, ng/g	<LOD	5.8 ± 0.3*	12.7 ± 0.7*
Spinach, ng/g	<LOD	40.1 ± 2.1*	23.1 ± 1.0*
Mint, ng/g	22 ± 0.9	10.7 ± 0.4*	4.8 ± 0.1*
Banana, ng/g	<LOD	34.1 ± 1.3*	12.4 ± 0.7*
Orange, ng/g	<LOD	7.9 ± 0.2*	3.2 ± 0.1*
Cherry, ng/g	<LOD	5.1 ± 0.3*	4.4 ± 0.1*
Apple, ng/g	<LOD	5.8 ± 0.3*	2.0 ± 0.08*
Watermelon, ng/g	<LOD	1.1 ± 0.05*	1.1 ± 0.04*
Melon, ng/g	<LOD	1.3 ± 0.02*	1.3 ± 0.04*

*μg g^{-1}.

Table 4
Comparative data from the literature on pre-concentration.

Method	Instrument	LOD, (ng mL^{-1})			Linear range, (ng mL^{-1})			Ref.
		Pb (II)	Mn (II)	Co (II)	Pb(II)	Mn(II)	Co(II)	
MWCNTs were chemically functionalized by glutaric dihydrazide	FAAS	0.17	–	0.16	5-160	–	5-140	(Tavallali et al., 2019)
Polythiophene nanocomposite-based air-agitated dispersive μSPE	FAAS	0.7	–	1.5	25-100	–	25-60	(Rajabi & Hemmati, 2021)
SPE using *Herpetocypris brevicaudata* loaded on Amberlite XAD-4 biosorbent	UV–VIS	–	0.94	1.4	–	3-670	3-670	(Topuz, Batmaz, Külkoylüoglu, & Çapraz, 2021)
A deep eutectic solvent microextraction	FAAS	2.4	1.0	4.6	5-60	2.5-25	5-30	(Soylak and Koksal, 2019)
SPE using 3-phenyl-1-(2-pyridyl) thiourea as sorbent	FAAS	0.79	–	–	–	–	–	(Uçak and Aydın, 2022)
SPE using *Bacillus cereus* loaded magnetic γ-Fe$_2$O$_3$ nanoparticles	ICP-OES	–	0.08	–	–	0.25-30	–	(Ozdemir et al, 2022)
SPE using Dowex 50 W-x8 and Chelex-100 resins	ICP-OES	–	–	0.08	–	–	10-70	(Nomngongo, Ngila, Msagati, & Moodley, 2013)
MSPE based on *R. brevipes* loaded γ-Fe$_2$O$_3$ magnetic nanoparticles	ICP-OES	0.022	0.015	0.024	0.025-20	0.025-20	0.025-20	This work

best values for preconcentrations of Pb(II), Mn(II), and Co(II). The developed method offers a number of benefits, including a high biosorption capacity, low cost, simplicity, quickness, and a high capacity for regeneration. By using the developed method, the sensitivity of ICP-OES was improved for Pb(II), Mn(II), and Co(II) ions. Ultimately, our method was successfully applied to determine Pb(II), Mn(II), and Co(II) ions from water, beverage, and food samples using ICP-OES. The use of the developed method as routine method is recommended for determination of target metals from natural samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2023.135608.

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