Microchimica Acta (2018) 185: 73
https://doi.org/10.1007/s00604-017-2605-5

ORIGINAL PAPER

Boletus edulis loaded with γ-Fe_2O_3 nanoparticles as a magnetic sorbent for preconcentration of Co(II) and Sn(II) prior to their determination by ICP-OES

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Received: 29 September 2017 / Accepted: 1 December 2017 / Published online: 20 December 2017

Abstract

The authors show that the fungus *Boletus edulis* loaded with γ-Fe_2O_3 nanoparticles is a viable sorbent for magnetic solid phase extraction of trace levels of Co(II) and Sn(II). The surface structure of immobilized magnetized *B. edulis* was characterized by FT-IR, SEM and EDX. Experimental parameters were optimized. Following elution with 1 M HCl, the ions were quantified by ICP-OES. The limits of detection are 21 pg·mL^{-1} for Co(II), and 19 pg·mL^{-1} for Sn(II). The preconcentration factors are 100 for both ions. The sorption capacities of the sorbent are 35.8 mg·g^{-1} for Co(II) and 29.6 mg·g^{-1} for Sn(II). The method was applied to the analysis of certificated reference materials and gave ≥95% recoveries with low RSDs. It was also successfully applied to the quantification of Co(II) and Sn(II) in spiked environmental and food samples.

Keywords Biosorbent · Magnetic solid phase extraction · Toxic metals · Trace analysis

Introduction

The back demand toxicity of metal ions to animals and humans is the subject of many researchers demonstrating the significance of the determination of these metals in food products [1, 2]. Heavy ions enter the human system by ingestion and inhalation, and entering via ingestion depends on nutrition habits. There is now expanding arguments of the significance of trace elements in human food. Many metal ions (such as Fe and Cu) are essential to protect metabolic activities in living systems; others (as Cd and Pb) are not essential and have no biological activities. It is well known that at high levels of the essential metals, they can be hazardous to living systems [3]. Hence, the detection of very low level of hazardous metal ions acts a progressively significant role in agriculture, food, industry, environment, etc. [4].

The determination of heavy metals at trace level usually requires prior preconcentration and/or separation stages in order to develop sensitivity [5]. Several preconcentration processes such as coprecipitation, flotation, liquid-liquid extraction, electrochemical deposition, cloud point extraction and ion-exchange, etc. [6, 7] have been utilized for the separation and preconcentration of trace metal ions.

Solid phase extraction (SPE) is an effective preconcentration and separation processes for metal ions because it has several significant superiorities such as economic, simplicity, rapid, flexibility, higher pre-concentration factors, low cost due to lower payment of reagents, lack of emulsion and

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00604-017-2605-5) contains supplementary material, which is available to authorized users.

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more environment-friendly. Many SPE substances have been successfully applied for separation and preconcentration of metal ions at very low levels [8].

γ-Fe_2O_3 is a sample of the widely utilized metal oxides as a nano-magnetic iron oxide. Nowadays, the application of magnetic nanoparticles, as a sorbent, for metal ions has received great attention in chemical and environmental engineering areas in order to figure out the consolidated problems with the separation operation from polluted fields. The great attention in magnetic nanomaterials is primarily because of their separation from the environment by utilization an outer magnetic field [9].

In this study, a novel magnetic solid phase bio-extractor based on the use of *Boletus edulis* loaded with γ-Fe_2O_3 nanoparticles was used for the preconcentration of Co(II) and Sn(II) from natural samples. Effects of important experimental parameters were investigated and the recommended method was validated and also applied for natural reel samples.

Materials and methods

Biological materials

In this study, *B. edulis* collected in Sülün, Afyonkarahisar, Turkey were used as the biological material.

Preparation of *B. edulis* for preconcentration and separation

Once the fungal samples have been collected, they were cleaned twice with distilled water to remove contaminants. After cleaning, it was dried at 25 °C for one week. Dried *B. edulis* were ground in a porcelain bowl to obtain a fine powder. It was then allowed to stand in the oven at 80 °C for 24 h to kill all of the fungal cells. Finally, *B. edulis* were inoculated with malt agar at 25 °C for 24 h. The absence of micelles of *B. edulis* gave a positive result, meaning that the fungus cells had completely died.

Synthesis of γ-Fe_2O_3 magnetic nanoparticles

γ-Fe_2O_3 magnetic nanoparticles was synthesized by method described in literature [10, 11] and detailed in S1.

Immobilization of *B. edulis* to γ-Fe_2O_3 magnetic nanoparticles

Approximately 0.1 g of the dried fungus were separately added to the aqueous suspension containing γ-Fe_2O_3 magnetic nanoparticles and refluxed at 65 °C for one hour. After filtration, the black precipitate was washed with pure water to neutrality and then dried at 90 °C for 24 h [10].

Preparation of column for magnetic solid phase extraction

Preparation of magnetic solid phase extraction column was described by method given in literature [12] and detailed in S2.

Sample preparation

The recommended method was validated by applying to certified reference samples: NWTM23.4 and NWTM-25.4 (water) which were available from laboratory. Tap water was sampled in Diyarbakır, Turkey. Mineral water, ice tea, orange juice and energy drink samples were bought from local markets. Procedures for sample preparation were detailed in our recent study [13].

Results and discussion

Surface studies

Surface macrostructures of *B. edulis* immobilized on γ-Fe_2O_3 nanoparticles, Co(II) on *B. edulis* immobilized on γ-Fe_2O_3 nanoparticles, Sn(II) on *B. edulis* immobilized on γ-Fe_2O_3 nanoparticles were investigated by SEM-EDX. By considering Supplemental Fig. S1, it can be concluded that a homogenous surface was obtained. Additionally, after immobilization of Co(II) and Sn(II), they were detected on *B. edulis* immobilized on γ-Fe_2O_3 nanoparticles by EDX. FT-IR was employed for investigation of surface functionalities. Results were comparatively presented in Supplemental Fig. S8. Fe–O vibrations of γ-Fe_2O_3 were observed on 697 and 592 cm^{-1} (Supplemental Fig. S2a). The peaks at 1021 and 1379 cm^{-1} may be arise from C-N stretching of amine and S = 0 stretching of sulfo functionalities of fungal surface, respectively. C=C stretching was recorded as peak at 1635 cm^{-1}. C-H stretching of alkane and alkenes were recorded at approximately 3000 cm^{-1}. From Supplemental Fig. S2b there was no significant difference after loading of Co(II). Major changes were observed after loading of Sn(II) (Supplemental Fig. S2c). Shifting on peaks were evaluated as complexation of metal ions with *B. edulis* immobilized on γ-Fe_2O_3 nanoparticles.

Effect of initial pH

The pH value of the reaction mixture has a very crucial effect on the biosorption of metal ions and solid phase extraction processes. The pH value affects the number of metal binding

sites on the biosorbent surface [13]. Every microorganism denotes varied biosorption properties at a given pH due to differences in the cell wall structure [14]. The effect of pH value of the contact solution on biosorption capacity values of metal ions was studied in the pH range of 2.0–9.0. The results of this study are presented in Supplemental Fig. S3. The maximum biosorption capacity values for both Co(II) and Sn(II) were observed at pH: 6.0. At low pH < 5.0, the biosorbent surface should be positive charge so that active binding sites lead to the inhibition of metal biosorption process [15, 16]. At high pH > 6.0, the biosorption efficiency for studied metal ions decreases due to the interaction of OH^- with the ions [17]. Our results are compatible with that of Kilinc et al. [18]. Thus, all further studies were conducted at pH: 6.0.

Effect of sample flow rate

The interaction of metal ions in solution with the biosorbent is influenced by the sample flow rate that is one of the factor affecting the length of time required for the determination of Co(II) and Sn(II) ions [19]. In this study, 50 mL of sample solution passing through *B. edulis* loaded iron nanoparticles with the different flow rate varying from 1.0 to 6.0 mL min^{-1} were investigated and quantitative recoveries of studied metal ions were obtained at sample flow rate of 3.0 mL min^{-1}. Supplemental Fig. S4 shows these results. At higher flow rates the efficiency of the biosorption was decreased, which suggests a less effective metal ions reagent interaction. Our findings in this study are supported by Karatepe and Soylak [20] . Therefore, all further studies were performed at 3 mL min^{-1} flow rates for sample solutions.

Effect of amount of *B. edulis*

The biosorbent amount is one of the most important parameters in the biosorption studies because it determines the capacity of the biosorbent for obtaining quantitative uptake of the analyte metal. It is obvious that with an increase in the amount of biomass, more surface area and greater number of binding sites are existing and thus the uptake of the analyte metal ions increases [13]. Under the selected optimum conditions, different amount of biomass ranging from 50 to 250 mg were experimented. It can be seen from Supplemental Fig. S5 that the biosorption ratio increased from 72.4% to 99.3% and 68.9% to 98.6% for Co(II) and Sn(II) respectively, with an increase in the amount of *B. edulis* from 50 to 100 mg. Co(II) and Sn(II) recovery reached at the point of plateau over the 150 mg amount of *B. edulis*. It was suggested that an increase in the amount of biomass may cause an increase in the electrostatic interactions between the cells to agglomerate, which contributes to a decrease in the number of binding sites available [21]. Therefore, 150 mg amount of *B. edulis* was used in all subsequent studies.

Effect of amount of γ-Fe_2O_3 magnetic nanoparticles

The amount of the support materials is very substantial parameter for the quantitative recoveries of the metal ions in solid phase extraction studies [13]. The quantitative retention of the Co(II) and Sn(II) ions were examined in relation to the amount of iron nanoparticles, which was varied from 50 to 300 mg. Supplemental Fig. S6 shows that the quantitative recoveries of Co(II) and Sn(II) ions were observed in the range of 100 mg. All further studies were applied at 100 mg amount of iron nanoparticles.

Effect of type, concentration and volume of the eluent

The selection of eluent is important in view of reusing the column without damage on the surface of solid phase extraction biomaterials [5]. For this purpose, different eluent solutions at various concentrations were evaluated for desorption of biosorbed Co(II) and Sn(II) ions from the *B. edulis* loaded iron nanoparticles column. The results are given in Table 1. It was determined that when the concentration of hydrochloric and nitric acid increased, the elution degrees also increased. According to the results, it is clearly indicated that quantitative elution was achieved when 5 mL of 1 mol L^{-1} HCl was used. The recovery value of Co(II) and Sn(II) ions in this condition was 100 ± 1.3 and 99.8 ± 0.7, respectively. These results agreed with that of Kilinc et al. [22]. A 5 mL amount of 1 mol L^{-1} HCl was used as the eluent for further experiments.

Effect of the sample volume

The solid phase extraction technique is applied to obtain high preconcentration factor and it is a common procedure for

Table 1 Effect of eluent type, volume and concentration on recoveries of Co(II) and Sn(II) by using immobilized *B. edulis*

Type of elution solution	Volume (mL)	Concentration (mol L^{-1})	% Recovery	
			Co(II)	Sn(II)
HCl	3	0.5	85.9 ± 0.8	83.1 ± 0.6
	5	0.5	92.7 ± 1.6	91.4 ± 0.9
	3	1	93.5 ± 1.4	92.9 ± 1.5
	5	1	100 ± 1.3	99.8 ± 0.7
HNO_3	3	0.5	81.9 ± 1.4	80.8 ± 1.2
	5	0.5	88.5 ± 0.8	87.9 ± 1.3
	3	1	89.7 ± 0.9	89.5 ± 1.1
	5	1	96.3 ± 0.7	95.7 ± 1.4

extraction and separation of metal ions from large sample volumes [23]. The effect of the sample volume of aqueous phase on the retention of Co(II) and Sn(II) ions on *B. edulis* loaded iron nanoparticle was investigated between 50 and 500 mL volume values. The results are shown in Supplemental Fig. S7. Both the Co(II) and Sn(II) ions are quantitatively recovered when using up to 500 mL of the sample solution. Therefore; a preconcentration factor of 100 can be achieved when 500 mL of the sample was used and the column with 5 mL of 1 mol L^{-1} HCl was eluated. Preconcentration factor was found as 100 by Oral et al. [24] when various immobilized biosorbents were used.

Effect of interference studies on the recoveries of co(II) and Sn(II)

During the determination of the metal ion concentration by analytical applications, some potentially interfering ions in analyzed samples are important problem [25]. To determine the possible effects of them on the biosorbent capacity it was studied and evaluated under the optimum conditions in presence of some potentially interfering ions such as Na(I), K(I), Ca(II), Mg(II), Fe(II), Al(III), Cd(II), Cu(II), Ni(II) and Zn(II). Table 2 demonstrates that a large number of ions tested have no substantial effect on the determination of analyte ions. Bakircioglu et al. [26] and Shegefti et al. [27] did not find any interference when different analyte ions and immobilized biosorbent were used.

Effect of column reuse

The reusability of the columns is like a key parameter in the view of the analytical and economical point [28]. The stability and potential recyclability of the column containing immobilized microbial biomass were evaluated by monitoring the change in the recoveries of the analyte ions. Supplemental Fig. S8 shows that a column loaded with magnetized *B. edulis* can be reused 30 cycles of sorption and desorption, with a recovery of >95%.

Table 2 Interference studies on recoveries of Co(II) and Sn(II) by using immobilized *B. edulis*

Ion	Interference to metal ion ratio	% Recovery[a]	
		Co(II)	Sn(II)
Na(I)	2000	98.5 ± 0.8	97.6 ± 0.9
K(I)	2000	97.7 ± 0.6	97.1 ± 0.5
Ca(II)	100	99.5 ± 0.5	98.8 ± 0.7
Mg(II)	50	98.7 ± 1.5	98.1 ± 0.9
Fe(II)	50	97.2 ± 1.3	96.5 ± 0.8
Al(III)	10	96.1 ± 1.1	95.6 ± 1.1
Cd(II)	5	97.3 ± 0.7	96.8 ± 1.2
Cu(II)	5	97.9 ± 1.4	96.4 ± 0.9
Ni(II)	5	98.1 ± 1.2	97.6 ± 0.8
Zn(II)	5	98.4 ± 0.6	97.8 ± 1.4

[a] Concentrations of the ions are 100 μg L^{-1}

Biosorption capacity

To examine the biosorption capacity of magnetically charged of *B. edulis*, 100 mL of 1 mg L^{-1} Co(II) and Sn(II) solutions at the best pH values were mixed with 50 mg *B. edulis* loaded with magnetic iron oxide nanoparticles at 120 rpm for 2 h at room temperature using a shaker. Before the determination of residual amounts of Co(II) and Sn(II) by ICP-OES, *B. edulis* loaded with magnetic iron oxide nanoparticles was separated from the solution using a magnet. The biosorption capacity of *B. edulis* loaded iron nanoparticles for Co(II) and Sn(II) was found as 35.8 mg g^{-1} and 29.6 mg g^{-1}, respectively. In addition, γ-Fe_2O_3 nanoparticles, without *B. edulis* immobilized, was also used at the best experimental conditions. The biosorption capacities for Co(II) and Sn(II) were found as 4.2 mg g^{-1} and 6.0 mg g^{-1}, respectively. The biosorption capacity for Co(II) ion was found as 4.3 mg g^{-1} by Tuzen et al. [29], for Sn(II) ion was found as 10.4 mg g^{-1} by Kilinc et al. [18], when different immobilized biosorbent were used. Our results show good performance than their results.

Analytical performance and application

Analytical features of the method were evaluated in view of LOD, LOQ, linear range, RSD, correlation coefficient and preconcentration factor. LOD was calculated according to the regulation by of IUPAC (3Sb/b where Sb is the standard deviation of blank and b is the slope of calibration graph) and LOQ was calculated from 10Sb/b. Analytical features of MSPE method based on *B. edulis*, immobilized γ-Fe_2O_3 nanoparticles for the preconcentration of Co(II) and Sn(II) are summarized in Table 3. Some analytical features of methods from the literature are summarized in Table 4 for preconcentration of Co(II) and Sn(II). It is clear to conclude

Table 3 Analytical performance of method

Parameter	Co(II)	Sn(II)
Linear range, ng mL^{-1}	0.2–10	0.2–20
Calibration equation (conc .as ng mL^{-1})	y = 13,363×-1373.2	y = 431.93× + 6.5791
r^2	0.9982	0.9987
LOD, ng mL^{-1}	0.021	0.019
LOQ, ng mL^{-1}	0.071	0.066
RSD, %	4.9	1.3
Loading capacity (mg g^{-1})	35.8	29.6
Preconcentration factor	100	100

Table 4 Comparative data from literature for the preconcentrations of Co(II) and Sn(II)

Method	Ion	Linearrange	LOD ng mL^{-1}	Instrument	Matrix	Ref.
SPE on resting eggs	Co(II)	–	41.4	FAAS	Water and soil	[30]
Preconcentration with dithizone functionalized graphene	Co(II)	0.01–3.0	13	XRF	Water	[31]
Ligand-less in situ surfactant-based SPE	Co(II)	3.0–300	1.0	FAAS	Water	[32]
MSPE on *Boletus edulis* loaded with γ-Fe_2O_3 nanoparticles	Co(II)	0.2–10	0.021	ICP-OES		This method
Optimized ultrasound-assisted temperature-controlled ionic liquid microextraction	Sn(II)	0.1–6.0	42	FAAS	Canned foods	[33]
Carrier element-free coprecipitation	Sn(II)	0.05–4.0	0.013	GF-AAS	Water and beverage	[34]
Flow-injection analysis (FIA) system incorporating a micro-column of ZrO_2	Sn(II)	–	0.07	ICP-OES	–	[35]
MSPE on *Boletus edulis* loaded with γ-Fe_2O_3 nanoparticles	Sn(II)	0.2–20	0.019	ICP-OES		This method

that the recommended method has over advantages such as simplicity, eco-friendly procedures, re-usability application in addition to low LOQ and wide linear range.

The recommended method was validated by applying to certified water samples. Results were in good agreement. Concentrations of Co(II) and Sn(II) in environmental and food samples were measured after MSPE procedure was applied. Results are presented in Table 5.

Conclusion

A new magnetic-bio solid phase extractor was prepared by using *B. edulis* and γ-Fe_2O_3 nanoparticles, which demonstrated excellent efficiency for preconcentrations of Co(II) and Sn(II) from environmental and food samples before their determinations. The detection limits of Co(II) and Sn(II) were 0.021 and 0.019 ng mL^{-1}, respectively under optimum conditions. Thus, sensitivity of ICP-OES was improved for Co(II) and Sn(II). The optimum MSPE conditions were found as being a pH 6.0; a sample flow rate of 3.0 mL min^{-1}; 150.0 mg of *B. edulis*; 100 mg of γ-Fe_2O_3 magnetic nanoparticles and 5.0 mL of 1 mol L^{-1} HCl as desorption solution for immobilized fungi. By considering the results it can be concluded that there was no major interferic ion that limits the method. The MSPE process was validated with two certificated reference materials and applied some real food and water samples. In addition to MSPE, *B. edulis* and γ-Fe_2O_3 nanoparticles can be used in batch method for routine purpose. Results indicated that this novel process demonstrates significant possible usage in real sample analysis in the hereafter.

Table 5 Application of the method to real samples

Sample	Co(II) μg mL^{-1}	Sn(II) μg mL^{-1}
NWTM-25.4, certified	27.5	23.8
NWTM-25.4,determined	26.8 ± 2.8	23.5 ± 1.9
NWTM-23.4, certified	7.09	2.79
NWTM-23.4,determined	7.01 ± 0.6	2.69 ± 0.2
Tap water	<LOD	<LOD
Tap water[a]	9.9 ± 0.7	9.8 ± 0.9
Tigris River water	2.2 ± 0.2	7.6 ± 0.6
Mineral water	<LOD	<LOD
Ice tea	2.8 ± 0.1	7.0 ± 0.3
Orange juice	4.0 ± 0.3	16.5 ± 1.1
Energy drink	1.3 ± 0.1	<LOD

[a] Spiked with10 μg mL^{-1} of Co(II) and Sn(II)

Compliance with ethical standards The authors declare that they have no competing interests.

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