



A magnetized fungal solid-phase extractor for the preconcentrations of uranium(VI) and thorium(IV) before their quantitation by ICP-OES

Ersin Kılınç¹ · Sadin Özdemir² · M. Serkan Yalçın³ · Mustafa Soylak^{4,5}

Received: 9 February 2019 / Accepted: 29 April 2019
© Springer-Verlag GmbH Austria, part of Springer Nature 2019

Abstract

The fungus *Bovista plumbea* immobilized on γ -Fe₂O₃ nanoparticles is shown to be a novel sorbent for magnetic solid-phase extractions of U(VI) and Th(IV). The biosorbent was characterized by FT-IR, SEM, and EDX. The effects of pH value, flow rate and volume of sample, amounts of biomass and support material, eluent type, foreign ions and repeated use of the sorbent on extraction efficiency were investigated. The sorption capacities are 41 and 44 mg g⁻¹, respectively, for U(VI) and Th(IV). The results indicated that *B. plumbea* immobilized onto γ -Fe₂O₃ nanoparticles can be utilized as a novel material for the preconcentrations of U(VI) and Th(IV) in certified materials and in spiked tap, river and lake waters.

Keywords Magnetic solid phase extraction · Uranium · Thorium · Preconcentration · *Bovista plumbea*

Introduction

Water pollution caused by radioactive elements is an issue that needs to be increasingly focused. The emergence of radioactive contamination is due to the increasing number of

industrial activities, including nuclear power plants, nuclear weapon testing, nuclear fuel-producing technologies, mining, and laboratories working with radioactive materials [1–3]. Nuclear spent fuel usually contains actinides such as thorium, uranium and various fission products [4].

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00604-019-3474-x>) contains supplementary material, which is available to authorized users.

In order to detection very low concentration of radioactive elements in water, several useful spectroscopic techniques have been used. However, a preconcentration step is also required before using these techniques to improve sensitivity [5]. Such methods being utilized for preconcentration are dispersive and/or conventional liquid-liquid microextraction, and solid phase extraction (SPE) etc. [6–9]. Among these methods, SPE is a more common application in respect to simplicity, flexibility, and efficiency [10, 11]. Because of cost-reduction, effective and promising sorbents from biological origin have attracted attention. From this point of view biomaterials based on bacteria, fungus, yeast, and algae greatly facilitate these expectations in the SPE process [12, 13].

✉ Ersin Kılınç
kilincersin@gmail.com

✉ M. Serkan Yalçın
serkanyalcin@mersin.edu.tr

¹ Department of Chemistry and Chemical Processing Technologies, Technical Science Vocational School, Dicle University, 21280 Diyarbakır, Turkey

² Food Processing Programme, Technical Science Vocational School, Mersin University, 33343 Mersin, Turkey

³ Department of Chemical and Chemical Processing Technologies, Technical Science Vocational School, Mersin University, 33343 Mersin, Turkey

⁴ Department of Chemistry, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey

⁵ Technology Research & Application Center (TAUM), Erciyes University, 38039 Kayseri, Turkey

The intent of this paper is to improve novel and simple method for the preconcentrations of thorium and uranium in environmental water samples after preconcentration on *B. plumbea* immobilized onto γ -Fe₂O₃ nanoparticles. Also, important experimental parameters were investigated and recommended method was validated and applied to environmental samples.

Materials and methods

Chemical reagents

Analytical grade chemicals were used in experiments. Standard metal solutions were supplied from Merck, Darmstadt-Germany, and diluted with lower concentrations with distilled water. CASS-4 and NWTM-15 as certified reference materials were available in laboratory. All laboratory glassware was cleaned with concentrated HNO_3 before use. All of the experiments were performed at least 3 times.

Instrumentation

Concentrations of U(VI) and Th(IV) were measured by ICP-OES (Perkin Elmer) at 385.958 and 283.730 nm. The solutions were passed through the 10 mm \times 100 mm filtration columns equipped with polypropylene frits using Waters Marlow 323 model peristaltic pump for SPE experiments.

Preparation of column for magnetic solid-phase extraction (MSPE)

Biomaterial, *B. plumbea* mushroom (Afyonkarahisar, Turkey) was cleaned carefully and dried. The dried biomaterial disintegrated using the blender was then ground to powder. Until all cells died, it was kept in an oven at 80 °C for 1 day.

$\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were synthesized by the method described in the literature [14]. Briefly, the required amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (mole ratio 2:1) were weighed and dissolved with pure water (30 mL). This solution was ultrasonicated for 5 min and refluxed at 65 °C for 10 min. Then, during a vigorous stirring, 20 mL of ammonia (10%, v/v) was added dropwise and the black precipitate observed. After 1.5 h, precipitation of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle was completed. To perform immobilization, 0.1 g dried *B. plumbea* added the suspension of nanoparticles. This suspension refluxed at 65 °C for 1 h. After the filtration, the black precipitate was washed and dried. Finally, this magnetically immobilized *B. plumbea* was applied to the column.

Preconcentration procedure

pH of 50 mL of 20 ng mL⁻¹ of interested ion solutions were adjusted before passing on *B. plumbea* immobilized onto $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles loaded SPE column by using peristaltic pump. After elution with diluted HCl, their concentrations were measured by ICP-OES.

Results and discussion

Surface functionalities

As can be seen from Supplemental Fig. S1a, the peak at 544 cm⁻¹ was attributed to the stretching vibration of Fe-O bond. The peaks at 1031 and 1372 cm⁻¹ might derive from C-N stretching of amine and S=O stretching of sulpho functionalities of biosorbent surface, respectively. The peak at 1635 cm⁻¹ was recorded to the C=C stretching. The broad peak at 3200 cm⁻¹ was attributed to the stretching of O-H group. The broad peak at 1326 cm⁻¹ was ascribed to complexation of Th(IV) with biosorbent surface (Supplemental Fig. S1b). Different peaks at Supplemental Fig. S1c at 1100–1600 cm⁻¹, were assigned to complexation of U(VI) with surface functionalities of *B. plumbea*. Also, SEM images showed that, biosorbent surface had homogenous structures (Supplemental Fig. S2a,b,c). Additionally, after biosorption of U(VI) and Th(IV), they were detected on *B. plumbea* immobilized onto $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles by EDX (Supplemental Fig. S3a,b,c).

Optimization of the method

The parameters pH value, flow rate, effect of amounts biosorbent and support material, effect of type and volume of eluent, effect of the sample volume were investigated.

The following parameters were optimized: Solution pH value, sample flow rate, amount of biosorbent and support material, eluent solution, sample volume. Respective text, tables, and figures on optimizations are given in the Electronic Supporting Material. In short, the following experimental conditions were found to give the best results: pH 4.0 (Supplemental Fig. S4), 3.0 mL min⁻¹ flow rate (Supplemental Fig. S5), 75 mg amount of *B. plumbea* on 50 mg amount of $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles (Supplemental Fig. S6a and b), 5.0 mL of 1.0 mol L⁻¹ HCl as eluent (Supplemental Table S1), and 600 mL of sample volume (Supplemental Fig. S7). For all further experiments, these optimal experimental conditions were used.

The effect of coexisting ions

Coexisting ions from the matrix may have interfered with the determination of analyte concentration by analytical methods. In this study, to examine whether such an effect exists it was investigated in the presence of some foreign ions including Na⁺, K⁺, Fe⁺², Mg⁺², Ca⁺², Cd⁺², Al⁺³, Co⁺², Mn⁺², Ni⁺², and Zn⁺². These ions were added individually to a solution containing the constant concentration of U(VI) and Th(IV). As seen in Table 1, the results indicated that foreign ions do not interfere with the recovery and determination of the analytes.

Table 1 Effect of matrix ions on SPE

Foreing Ions	Interference to metal ion ratio	Recovery,% ^a	
		Th(IV)	U(VI)
Na ⁺	2000	96.3 ± 0.6	97.2 ± 1.3
K ⁺	2000	97.1 ± 1.4	97.8 ± 0.9
Ca ⁺²	50	98.9 ± 0.6	99.3 ± 1.2
Mg ⁺²	50	97.3 ± 1.2	98.3 ± 1.5
Fe ⁺²	25	95.6 ± 1.8	97.1 ± 0.9
Al ⁺³	10	95.3 ± 0.9	96.7 ± 1.4
Cd ⁺²	5	96.8 ± 1.3	97.4 ± 1.6
Co ⁺²	5	95.2 ± 1.1	97.6 ± 1.7
Mn ⁺²	5	96.4 ± 0.7	96.9 ± 1.2
Ni ⁺²	5	97.1 ± 0.3	98.3 ± 1.5
Zn ⁺²	5	96.6 ± 1.5	97.1 ± 1.2

^a Concentrations of the metal ions are 100 µg L⁻¹

Biosorption capacity and column reusability

The usage of biological substances for the preconcentration and separation of traces of metals and some organic materials at trace levels is popular due to good biosorption properties such as high surface area and high biosorption capacities for biological substances.

To the best of our knowledge, there has not been enough reported investigation on the usage of immobilized fungal biomass as a biosorbent material for preconcentration of heavy metals. When checked the literature, there was not any study with immobilized *B. plumbea* using SPE methods. This is also important for the originality of the investigation.

Determination of the biosorption capacity of the biosorbent is important because of the quantitative determination of how much biosorbent is required [5, 15]. For this aim, the experiments applied in the batch mode (100 mL of 100 mg L⁻¹ of U(VI) and Th(IV) was added to sorbent composed of 75 mg biosorbent and 50 mg support material) under the best conditions. After the experiments, the biosorption capacities of

B. plumbea immobilized onto γ-Fe₂O₃ nanoparticles were found as 40.6 and 43.9 mg g⁻¹ for U(VI) and Th(IV), respectively.

The potential reusability and stability of the SPE column packed with *B. plumbea* immobilized onto γ-Fe₂O₃ nanoparticles were evaluated after several adsorption-desorption cycles. It was found that the recoveries of analytes were higher than 95% even after 30 cycles (Supplemental Fig. S8).

To understand the mechanism of adsorption, 100 mL of metal ions at the concentration interval of 50–150 mg L⁻¹ were added with 1250 mg of biosorbent composed of 75 mg *B. plumbea* and 50 mg of γ-Fe₂O₃ nanoparticles. The results were applied to Langmuir and Freundlich models. r² were obtained as 0.9926 and 0.9970 for U(VI) and Th(IV) in Langmuir model while they were lower than 0.9900 for Freundlich model. By considering the results it could conclude that single layer adsorption was efficient in this process. No lateral interaction is available between the adsorbed molecules, thus the heat of adsorption is constant and independent of coverage. The adsorbed metal ions remains at the site of *B. plumbea* immobilized onto γ-Fe₂O₃ nanoparticles until it is desorbed. As values were calculated as 119.0 and 106.4 mg g⁻¹ for U(VI) and Th(IV) from Langmuir equations.

The r² values in Tables 2 indicate that the adosprtion mechanisms of U(VI) and Th(IV) on *B. plumbea* immobilized onto γ-Fe₂O₃ nanoparticles followed the pseudo-second-order kinetic model. The pseudo second-order kinetic constant and the theoretical q_e by a type 1 pseudo second-order expression can be calculated from the plots of t/q_t versus t. In addition q_{e2} values were calculated as close to experimental ones. In this case, the electron coordination between the adsorbent and metal ions or adsorption through electron exchange concludes.

Analytical features and applicability

By applying the best experimental conditions, the analytical performance of the method was investigated. Analytical parameters were presented in Table 3. Linear calibration plots

Table 2 Kinetic parameters obtained from pseudo-first-order (q_{e1}: mg/g, k₁: min⁻¹) and pseudo-second-order (k₂: g/mg.min, q_{e2}: mg/g) for Th(IV) and U(VI)

Metal	Temp., °C	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		k ₁	q _{e1}	r ²	k ₂	q _{e2}	r ²
Th(IV)	25	0.0040	76.51	0.9066	0.0009	45.87	0.9915
	35	0.0041	72.66	0.9073	0.0015	46.08	0.9895
	55	0.0048	73.65	0.8863	0.0008	52.63	0.9897
	60	0.0053	71.88	0.8687	0.0008	56.49	0.9881
U(VI)	25	0.0044	74.80	0.9238	0.0011	48.07	0.9903
	35	0.0051	74.39	0.9223	0.0009	52.91	0.9909
	55	0.0054	72.81	0.9002	0.0010	54.34	0.9920
	60	0.0055	71.76	0.9118	0.0011	55.55	0.9921

Table 3 Analytical features of the method

Parameter	Th(IV)	U(VI)
LOD, ng mL ⁻¹	0.023	0.019
LOQ, ng mL ⁻¹	0.078	0.063
Linear range, ng mL ⁻¹	0.16–8.33	0.16–8.33
r ²	0.9941	0.9945
RSD	4.2	3.5
Preconcentration factor	120	120

were obtained between the ranges of 0.16–8.33 ng mL⁻¹ for U(VI) and Th(IV). A 120-fold preconcentration factor (PF) was acquired by considering 600 mL initial and 5.0 mL final volume. Limit of detections (LODs) were calculated as 0.023, 0.019 ng mL⁻¹, respectively for U(VI) and Th(IV). Analytical features of proposed method were also compared with other preconcentration procedures in the literature. Some analytical features are summarized in Table 4. It is clear to conclude that the presented method has over advantages including simplicity, re-usability application, green chemistry procedures in addition to low limit of quantitation (LOQ) and wide linear range.

To show the applicability of the method, it applied to environmental and tap water samples in addition to certified reference samples CASS-4 (Nearshore Seawater reference material for trace element) and NWTM-15 (fortified water). Satisfactory results were achieved for certified reference samples U(VI) and Th(IV) concentrations were lower than LOD for other samples in excluding water sampled from Van Lake. Additionally, spiked amounts of U(VI) and Th(IV) were detected quantitatively (Table 5).

Conclusion

The use of *B. plumbea* as a new biosorbent for the preconcentration of U(VI) and Th(IV) was presented. *B. plumbea* has provided the higher sorption capacity and mechanical strength after immobilized onto γ -Fe₂O₃ nanoparticles. Adsorption mechanism was investigated in details. The recommended method was validated by applying to certified reference materials with convincing results. In conclusion, it may use as a potential application in environmental water samples for U(VI) and Th(IV) removal.

Table 4 Comparative data from the literature for the preconcentrations of Th(IV) and U(VI)

Method	Ion	Linear range ng mL ⁻¹	LOD ng mL ⁻¹	Instrument	Matrix	Ref.
Modified mesoporous silica (MCM-41) using 5-nitro-2-furaldehyde	Th(IV) and U(VI)	–	0.30 and 0.30	ICP-OES	Water	[16]
SPE on Amberlite XAD-2000 resin loaded with -benzoin oxime	Th(IV) and U(VI)	200–3500	0.54 and 0.50	UV-vis	Water, ceramic samples	[17]
SPE using Merrifield chloromethylated resin anchored with calix[4]arene-o-vanillinsemicarbazone	Th(IV) and U(VI)	20–3400 and 100–15,000	4.29 and 6.14	ICPAES	Water, monazite sand, geological materials	[18]
The crystalline/amorphous hybrid material, namely UiO-66-NH ₂ /Urea-POP, as a new and highly efficient sorbent for SPE	U(VI)	0.005–2.0 mg L ⁻¹	0.6	UV-vis	Water	[19]
Preconcentration by ion-imprinted polymer-ternary complexes	U(VI)	2–50	0.7	UV-vis	River, lake and ground water	[20]
A novel method based on aeration-assisted homogeneous liquid–liquid microextraction using high density solvent	Th(IV) and U(VI)	0.3–550.0 and 0.5–600 ng L ⁻¹	0.09 and 0.12	ICP-MS	Water, hair samples	[8]
MSPE on <i>Bovista plumbea</i> loaded with γ -Fe ₂ O ₃ nanoparticles	Th(IV) and U(VI)	0.16–8.33	0.023 and 0.019	ICP-OES	Water	This method

Table 5 Th(IV) and U(VI) preconcentration in real samples

Sample	U(VI)		Th(IV)	
	Certified ng mL ⁻¹	Found ng mL ⁻¹	Certified ng mL ⁻¹	Found ng mL ⁻¹
CASS-4	3.0	2.95 ± 0.21	–	<LOD
NWTM-15	14.5	14.1 ± 0.9	–	<LOD
Tap water, Mersin	–	<LOD	–	<LOD
Tap water, Mersin ^a	–	4.9 ± 0.3	–	5.0 ± 0.3
Tap water, Diyarbakır	–	<LOD	–	<LOD
Tigris River water, Diyarbakır	–	<LOD	–	<LOD
Van Lake water, Van	–	76.2 ± 4.1	<LOD	<LOD

^a Spiked with 5.0 ng mL⁻¹ of Th(IV) and U(VI)

Acknowledgements The authors thank to Technology Research & Application Center (TAUM), Erciyes University, Kayseri-Turkey for SEM and FTIR Analysis.

Compliance with ethical standards The author(s) declare that they have no competing interests.

References

- Salameh SIY, Khalili FI, Al-Dujaili AH (2017) Removal of U(VI) and Th(IV) from aqueous solutions by organically modified diatomaceous earth: evaluation of equilibrium, kinetic and thermodynamic data. *Int J Miner Process* 168:9–18
- Ilaiyaraja P, Deba AKS, Sivasubramanian K, Ponrajub D, Venkatramana B (2013) Adsorption of uranium from aqueous solution by PAMAM Dendron functionalized styrene divinylbenzene. *J Hazard Mater* 250–251:155–166
- Humelnicu DG, Dinu MV, Dragan ES (2011) Adsorption characteristics of UO₂²⁺ and Th⁴⁺ ions from simulated radioactive solutions onto chitosan/clinoptilolite sorbents. *J Hazard Mater* 185: 447–455
- Sasmaz A, Yaman M (2008) Determination of uranium and thorium in soil and plant parts around abandoned lead–zinc–copper mining area. *Commun Soil Sci Plant Anal* 39:2568–2583
- Ozdemir S, Oduncu MK, Kılınç E, Soylak M (2018) Comparative solid phase extraction study on the U(VI) preconcentration by using immobilized thermotolerant *Bacillus vallismortis* and *Bacillus mojavensis*. *J Radioanal Nucl Chem* 315:185–193
- Hosseini SH, Rahmani-Sani A, Jalalabadi Y, Karimzadeh M, Hosseini-Bandegharai A, Kharghani K, Allahabadi A (2015) Preconcentration and determination of ultra-trace amounts of U(VI) and Th(IV) using titan yellow impregnated Amberlite XAD-7 resin. *Int J Environ Anal Chem* 95:277–290
- Lago AC, Lima GC, Wisniewski C, Nascimento MRL, Fadini PS, Luccas PO (2015) Determination of uranium in environmental water by flow injection analysis using a hybrid-imprinted polymer. *Anal Lett* 48:2739–2753
- Veyseh S, Niazi A (2016) A novel aeration-assisted homogenous liquid–liquid microextraction for determination of thorium and uranium in water and hair samples by inductively coupled plasma-mass spectroscopy. *Talanta* 147:117–123
- Dadfarnia S, Shabani AMH, Shakerian F, Esfahani GS (2013) Combination of solid phase extraction and dispersive liquid–liquid microextraction for separation/preconcentration of ultra trace amounts of uranium prior to its fiber optic-linear array spectrophotometry determination. *J Hazard Mater* 263:670–676
- Azzouz A, Kailasa SK, Lee SS, Rascon AJ, Ballesteros E, Zhang M, Kim K-H (2018) Review of nanomaterials as sorbents in solid-phase extraction for environmental samples. *Trends Anal Chem* 108:347–369
- Andrade-Eiroa A, Canle M, Leroy-Cancellieri V, Cerda V (2016) Solid-phase extraction of organic compounds: a critical review. *TrAC Trends Anal Chem* 80:641–654
- Hemmati M, Rajabi M, Asghari A (2018) Magnetic nanoparticle based solid-phase extraction of heavy metal ions: a review on recent advances. *Microchim Acta* 185:160–192
- Ozdemir S, Okumuş V, Dündar A, Kılınç E (2013) Preconcentration of metal ions using microbacteria. *Microchim Acta* 180:719–739
- Kilinc E (2016) γ -Fe₂O₃ magnetik nanoparticle functionalized with carboxylated multiwalled carbon nanotube: synthesis, characterization, analytical and biomedical application. *J Magn Magn Mater* 401:949–955
- Dev K, Rao GN (1995) Preparation and analytical properties of a chelating resin containing bicine groups. *Talanta* 42:591–596
- Yousefi SR, Ahmadi SJ, Shemirani F, Jamali MR, Salavati-Niasari M (2009) Simultaneous extraction and preconcentration of uranium and thorium in aqueous samples by new modified mesoporous silica prior to inductively coupled plasma optical emission spectrometry determination. *Talanta* 80:212–217
- Jahan B, Zolfonoun GE (2010) Simultaneous spectrophotometric determination of trace amounts of uranium, thorium, and zirconium using the partial least squares method after their preconcentration by -benzoic oxime modified Amberlite XAD-2000 resin. *Talanta* 80:1191–1197
- Jain VK, Pandya RK, Pillai SG, Shrivastav PS (2006) Simultaneous preconcentration of uranium(VI) and thorium(IV) from aqueous solutions using a chelating calix[4]arene anchored chloromethylated polystyrene solid phase. *Talanta* 70:257–266
- Fotovat H, Khajeh M, Oveisi AR, Ghaffari-Moghaddam M, Daliran S (2018) A hybrid material composed of an amino-functionalized zirconium-based metal-organic framework and a urea-based porous organic polymer as an efficient sorbent for extraction of uranium(VI). *Microchim Acta* 185:469
- Bicim T, Yaman M (2016) Sensitive determination of uranium in natural waters using UV-vis spectrometry after Preconcentration by ion-imprinted polymer-ternary complexes. *J AOAC Int* 99:1043–1048

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.