Preconcentration of Sn in Real Water Samples by Solid Phase Extraction Based on the Use of *Helvella leucopus* as a Fungal Biomass Prior to its Determination by ICP-OES

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INTRODUCTION

It has been reported that the toxicity and biological activity of tin (Sn) depends on its oxidation states (mainly Sn^{2+} and Sn^{4+}) (1, 2). Among them, Sn^{2+} is reported to be more toxic than Sn^{4+} . In addition, organotin compounds such as tributyltin, dibutyltin, and monobutyltin are also toxic (1). The concentration of total Sn in water samples is known to be at the ng mL^{-1} levels (3). From this perspective, the development of sensitive and selective analytical methods for the preconcentration of Sn^{2+} is an important issue in analytical and environmental chemistry. The direct determination of Sn by flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) is limited due to the poor sensitivity of these techniques and a preconcentration procedure is generally required before instrumental detection. Cloud point extraction (CPE) (4, 5), solid phase extraction (SPE) (1, 6-8), coprecipitation (3), and liquid-liquid extraction (9) allow the detection of tin. However, they require the use of chemical ligands and time-consuming steps such as centrifugation. Hydride generation for volatile stannane formation (10) and the electrothermal atomizer (11) are also employed for ultratrace deter-

ABSTRACT

Recently, biosorbents of biological origin such as fungus, algae, and bacteria have found special application as packing material in solid phase extraction (SPE). In this study, an alternative SPE method was developed and validated for the preconcentration of Sn prior to its determination by inductively coupled plasma optical emission spectrometry (ICP-OES). *Helvella leucopus*, a fungal biomass, was used as the biosorbent in the column studies. Experimental parameters, such as pH and flow rate of the solution, amounts of biosorbent and resin, and volume of the sample solution which affects the analytical results, were investigated. Effects of possible interfering ions on the SPE preconcentration of Sn were investigated. The sensitivity of ICP-OES was improved 47.1 times for Sn. The LOD and LOQ values were 0.06 and 0.21 ng mL^{-1} , respectively. Linearity was obtained in the concentration range of 1.0–30 ng mL^{-1} for Sn. The loading capacity of *Helvella leucopus* immobilized Amberlite XAD-4 was 10.4 mg g^{-1} . The concentrations of Sn in the water samples from the Tigris River were determined using the developed method and validated by analysis of the certified reference material NWTM-26.3 Fortified Water sample.

ety of samples. The advantages and disadvantages of the preconcentration techniques were evaluated in a recent review in detail (12). As an alternative to chemical ligands, the use of bacterial biomass materials has become of special interest due to their efficiency, surface functionality, environmentally friendly properties, and applicability for the preconcentration of metal ions. In addition, synthesis procedures for ligands are eliminated when biomass is used as the sorbent. However, methods for the preconcentration of Sn were focused on the sorption of batch conditions (13), SPE on ligands (6-8), CPE (2, 4, 5, 14), coprecipitation (3), and solvent extraction (9). Reports on the use of preconcentration methods for Sn using biomass are still very few.

In our research group, bacterial biomass immobilized to resin was used as a solid phase sorbent for the preconcentration of metal ions. In previous reports, *Geobacillus thermoleovorans subsp. stromboliensis*, immobilized on Amberlite XAD-4, was used for the preconcentrations of Cd and Ni before their detections by FAAS (15). *Bacillus sp.*, immobilized on Amberlite XAD-4 resin, was used as a biosorbent for solid phase preconcentration of Th prior to UV-Vis spectrometry determination (16). *Geobacillus thermoleovorans*, immobilized on Amberlite XAD-4 resin, was used as a biosorbent for solid phase preconcentration of U^{6+} prior to its spectrophotometric determination (17). Cd^{2+} and Co^{2+}

minations of Sn. SPE is the most common technique generally used for the preconcentration of metal ions, including toxic ions in a vari-

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were preconcentrated on *Pleurotuseryngii*, immobilized on Amberlite XAD-16, and their concentrations were determined by ICP-OES (18). Since preconcentration of Sn by the SPE method based on the use of fungal biomass is limited, in this study we focused on the development of a sensitive and selective preconcentration method. *Helvella leucopus* was used as the fungal biomass for the preconcentration of Sn prior to its determination by ICP-OES. Important experimental parameters were optimized throughout the study.

EXPERIMENTAL

Instrumentation

A Model Optima™ 2100 DV inductively coupled plasmaoptical emission spectrometer (ICP-OES) (PerkinElmer, Inc., Shelton, CT, USA) was used for the determination of Sn at the wavelength of 189.927 nm. The operating conditions of the ICP-OES for the determination of Sn were given in our previous study and are also listed in Table I (18). A Model MPC 227 digital pH meter (Mettler-Toledo Co., Columbus, OH, USA) was used for adjustment of the acidity of the solutions. Filtration columns (1.0 cm × 10.0 cm), equipped with polypropylene frits, were used for solid phase extraction (SPE). A Model Marlow 323 peristaltic pump (Waters Co., Milford, MA, USA) was used for passing the solutions through the column.

Standard Solutions and Reagents

Stock solutions of Sn were prepared from its individual stock solution at the concentration of 1000 µg mL⁻¹ (High Purity Standards, Charleston, SC, USA) with doubly distilled. This solution was used for the standards at lower concentrations. All glass materials were washed with 1.0 mol L⁻¹ of nitric acid and then with doubly

distilled water before use. HNO₃ (65%) and H₂O₂ (35%) were supplied from E. Merck (Darmstadt, Germany) and used in the digestion procedures. Amberlite XAD-4 (Sigma Chemical, USA, 20–40 mesh, 780 m²/g) was used as a substrate for the immobilization of *Helvella leucopus* and HCl (4.0 mol L⁻¹) was used to remove the contaminants from the Amberlite XAD-4. The resin was first rinsed with distilled water until its pH was neutral, then with an ethanol-water (1:1) solution, finally with distilled water again, and stored in a polyethylene bottle. Certified reference material NWTM-26.3 Fortified Water sample was purchased from LGC (Middlesex, UK).

Preparation of SPE Column

In this study, *Helvella leucopus*, collected from Siirt, Turkey, was used as a biosorbent for the preconcentration of Sn. To remove the dirt

from the biosorbent, it was washed twice with distilled water. After washing, the biosorbent was dried at 25 °C. The dried fungus was granulated in a porcelain mortar to achieve a fine powder, then oven-dried at 80 °C for 24 hours to assess the complete death of the dried cells. Finally, the cells were inoculated to malt agar at 25 °C for 24 hours. The absence of mycelia of *Helvella leucopus* showed positive results, meaning the complete death of the fungus. The SPE column was prepared by a procedure from our previous studies (15, 17). A 150-mg amount of dry powder biosorbent was mixed with 750 mg Amberlite XAD-4. After immobilization of the biosorbent to resin, it was sieved to get sizes of 20-60 mesh and packed in a solid phase column (1.0 cm x 10 cm). Before use, approximately 10 mL of 1.0 mol L⁻¹ HCl solution and 10 mL of doubly distilled deionized water were passed through the column for conditioning and cleaning.

TABLE I
ICP-OES Operating Conditions

Parameters	
RF power	1450 W
Plasma gas flow rate	15 L/min
Auxiliary gas flow rate	0.2 L/min
Nebulizer gas flow rate	0.8 L/min
Sample flow rate	1.5 L/min
View mode	Axial-Radial
Read	Peak area
Source equilibration time	15 sec
Read delay	60 sec
Replicates	3
Background correction	2-point (manual point correction)
Spray chamber	Scott-type spray chamber
Nebulizer	Cross-Flow GemTip Nebulizer (HF resistant)
Detector	CCD
Purge gas	Nitrogen
Shear gas	Air
Gas	Argon
Analytical wavelength	Sn 189.927 nm

Loading Capacity of *Helvella leucopus* Immobilized on XAD-4

The biosorption capacity of *Helvella leucopus* immobilized on XAD-4 resin for Sn^{2+} was found from experiments in batch conditions. An amount of 150 mg of *Helvella leucopus*, immobilized on 750 mg of Amberlite XAD-4, was added to 250-mL Erlenmeyer flasks containing 100 mL of 100 mg L^{-1} of Sn^{2+} , then it was agitated at 120 rpm for two hours. The temperature was kept constant at 25 °C during the batch adsorption studies. The immobilized biosorbents were then centrifuged at 10,000 rpm for 10 minutes. The supernatant and pellet (after acid digestion by concentrated HNO_3 acid) were used to determine the residual metal concentration by ICP-OES. The amount of biosorbed Sn^{2+} was calculated using the equation given in the literature (19) as follows:

$$q_{\text{eq}} = \frac{(C_0 - C_{\text{eq}}) V}{x}$$

where C_0 is the initial concentration of the solution, C_{eq} the concentration of the solution at equilibrium, V the volume of the solution, and x the mass of the biosorbent.

Preparation of Samples for SPE Procedure

The batch process was used to determine the biosorption capacity of *Helvella leucopus*, immobilized on XAD-4 resin. A 150-mg amount of *Helvella leucopus*, immobilized on 750 mg of XAD-4 resin, was added to 100 mL of solution containing 100 $\mu\text{g mL}^{-1}$ of Sn^{2+} solution at pH 6.0, and then incubated by shaking at 120 rpm for two hours. The biosorption capacity of immobilized *Helvella leucopus* was found at 10.4 mg Sn^{2+} per g of biosorbent.

The water samples were collected from three different locations of the Tigris River (Hevsel, Ongözlü, and Dicle Köprü). Before sampling, the polyethylene sample containers

were cleaned with 1.0 mol L^{-1} of HNO_3 and rinsed with distilled water. A 1.0 L amount of the water sample was added and filtered through a 0.45 μm membrane filter. Then, 1.0 mL of HNO_3 was added to prevent precipitation.

RESULTS AND DISCUSSION

Effects of pH

It is well known that with SPE experiments the sample solution pH is an important parameter for quantitative recoveries of the analyte metal ions on the biosorbent (20, 21). When the solution pH decreases, the protons compete with the metal ions for the binding sites of the biosorbent; but when the pH increases, the hydroxide will complex and precipitate the metal ions. From that point of view, the solution pH is the first parameter that should be optimized (22).

As shown in Figure 1, the effects of solution pH on the recoveries of Sn^{2+} on *Helvella leucopus*, immobilized on XAD-4 resin, were studied between the 2.0–8.0 range. It was found that 10.0 ng mL^{-1} of Sn^{2+} was quantitatively recovered at the pH range of 4.0–7.0. When the solution pH increased from 2.0 to 5.0, the Sn^{2+} recovery increased from 29.1% to 93.9%, respectively. These values may be due to the competition between the protons and analytes for the biosorption sites of the

immobilized biosorbent (18). Optimum recovery of Sn^{2+} was achieved at pH 6.0. On the other hand, when the solution pH increased from 6.0 to 8.0, the percentage of Sn^{2+} recovery decreased from 100% to 94.3% for *Helvella leucopus*, immobilized on the XAD-4 resin, respectively. The decrease in percentage of Sn^{2+} recovery at higher pH values may be attributed to the formation of anionic hydroxide complexes and to the competition between the cell wall and ammonia (23). Subsequent studies were carried out at an initial pH of 6.0.

Effect of Sample and Elution Flow Rates

The effect of the quantitative uptakes of the analyte metal ions in solid phase extraction processes depends on the flow rates of the sample and eluent solutions (24). The flow rate of the sample and elution solution is one of the most important parameters affecting both the uptake of the analyte metal ions and controlling the time of analysis (25). The effect of sample and eluent flow rate on the recovery of 10.0 ng mL^{-1} of Sn^{2+} is shown in Table II. It was found that in the flow rate range of 1.0–6.0 mL min^{-1} , the uptake of analyte metal ions was affected by the immobilized biosorbent. The optimum flow rate of the solution was 3.0 mL min^{-1} . At flow rates higher

Fig. 1. Effect of pH on the recovery of 10.0 ng mL^{-1} of Sn^{2+} .

than 3.0 mL min⁻¹, the uptake efficiency decreased because of insufficient phase contact between the Sn²⁺ and the binding sites of the biosorbent (24).

The effect of eluent (1.0 mol L⁻¹ HCl) flow rate on the recovery of 10.0 ng mL⁻¹ of Sn²⁺ was studied at the concentration of 1.0 mol L⁻¹ HCl (5.0 mL). Maximum uptake was obtained at flow rates between 1.0 and 2.0 mL min⁻¹. At eluent flow rates higher than 2.0 mL min⁻¹, the uptake efficiency of Sn²⁺ ions was not quantitative. All subsequent studies were carried out at a flow rate of 3.0 and 2.0 mL min⁻¹ for the sample and eluent solutions, respectively.

Effect of Amount of Biosorbent and Resin

The biosorbent and resin amount are one of the other important parameters for obtaining quantitative uptake of the analyte metal ions in solid phase extraction studies. It is obvious that with an increase in biosorbent, greater surface area and replaceable sites are available and thus the uptake of the analyte metal ions goes up (26). The effect of amount of biosorbent and resin dosage on the recovery of 10.0 ng mL⁻¹ of Sn²⁺ can be seen in Table III. The results show that the optimum amount of biosorbent within the experimental range of 100 to 400 mg was 300 mg, while 400 mg did not increase the uptake

efficiency. This may be due to the fact that a higher dose causes particle aggregates and interference or repulsive forces between the binding sites and, therefore, decreases the interaction of the metal ions with the biosorbent and reduces the total surface area of the biosorbent (27).

Support materials are required to have some physical adequacies such as high surface area, enough pore size to immobilization of biosorbent, and low particle size. In order to determine the effect of the dosage of XAD-4 resin on the quantitative uptake of Sn²⁺, studies were conducted with XAD-4 resin ranging in the amount from 200 to 1250 mg. The results showed that maximum uptake of Sn²⁺ was achieved at the concentration of 10.0 ng mL⁻¹ with an increase in

XAD-4 up to 750 mg. For further studies, 750 mg of XAD-4 was used because of the higher surface area at high dosage of biosorbent.

Effect of Eluent Type and Concentration

Non-destructive uptake is necessary for the regeneration of the biosorbent for reuse in successive biosorption and desorption cycles. To determine the non-destructive uptake, the concentration of eluent solution utilized for stripping the metals bound to the biosorbent surface must be as low as possible (28). Different concentrations of HCl and HNO₃ were used for the eluate of Sn²⁺ from *Helvella leucopus* immobilized on XAD-4 resin. The experimental results in Figure 2 show that 1.0 mol L⁻¹ HCl was sufficient for quantitative elution

Fig. 2. Effect of the type and volume of elution solutions on the recovery of 10.0 ng mL⁻¹ of Sn²⁺.

TABLE II

Effect of Flow Rate of Sample and Eluent Solution on Solid Phase Extraction of 10.0 ng mL⁻¹ of Sn²⁺

Sample Flow Rate (mL min ⁻¹)	Recovery (%)	Eluent Flow Rate (mL min ⁻¹)	Recovery (%)
1.0	99.3	1.0	98.9
2.0	96.5	2.0	99.1
3.0	98.8	3.0	96.8
4.0	93.8	4.0	95.2
5.0	86.2	5.0	86.1
6.0	80.7	6.0	83.7

TABLE III

Effect of Amounts of Biosorbent and Resin on the Recovery of 10.0 ng mL⁻¹ of Sn²⁺

Amount of Biosorbent (mg)	Recovery (%)	Amount of Resin (mg)	Recovery (%)
100	84.6	200	63.2
150	90.4	300	72.4
200	96.5	400	85.8
250	97.1	500	92.7
300	96.7	750	98.6
350	95.1	1000	97.3
400	95.0	1250	97.1

(>95%). The influence of eluent volume (1.0–10 mL, 1.0 mol L⁻¹ HCl) on the uptake of 10.0 ng mL⁻¹ of Sn²⁺ by *Helvella leucopus* immobilized on XAD-4 resin was studied. It was determined that quantitative uptakes were achieved for Sn²⁺ with 5.0 mL of 1.0 mol L⁻¹ HCl (98.8%), which is the amount of eluent used in further studies.

Effect of Sample Volume

For preconcentration of metal ions in a real sample, the sample volume is important for obtaining high preconcentration factors (29). In order to deal with real samples containing very low concentrations of metal ions, trace metal ions or radionuclides, the maximum applicable sample volume must be determined (30). From that point of view, the influence of the sample

TABLE IV
Effect of Volume of Initial Solution on the Recovery of 10.0 ng mL⁻¹ of Sn²⁺

Volume	Conc. (ng mL ⁻¹)	Recovery (%)
25	100.0	100.0
50	50.0	99.9
100	25.0	98.1
200	15.5	97.6
250	10.0	96.3
400	6.25	89.8

TABLE V
Analytical Figures of Merit of the SPE Method

Parameter	ICP-OES	SPE-ICP-OES
Linear range (ng mL ⁻¹)	50–1500	1.0–30
LOD (ng mL ⁻¹)	3.9	0.06
LOQ (ng mL ⁻¹)	13	0.21
RSD (%)	8.1	6.6
Slope	6.9	325
Intercept	-130	-142
r ²	0.9996	0.9997

volume on the uptake of Sn²⁺ was studied under optimum conditions (pH, eluent, etc.). The results in Table IV show that the uptake of Sn²⁺ was quantitative for volumes of 50–250 mL. At higher volumes, the uptake of Sn²⁺ decreased. The uptake value for a 400-mL sample volume was determined as 89.8%. Therefore, the preconcentration factor of 50 was obtained for an elution volume of 5.0 mL and sample volume of 250 mL.

Analytical Figures of Merit

In solid phase extraction studies, the potential regeneration and stability of the column is a very important parameter to evaluate the biosorbent which can guarantee its widespread application in industry. The stability of the solid phase extraction column shows that the uptake of Sn²⁺ ion was stable up to at least 30 biosorption-elution cycles with the recovery for the Sn²⁺ ions greater than 95.0% (Figure 3).

The analytical figures of merit of the developed SPE method are presented in Table V. The limit of detection (LOD) and limit of quantification (LOQ) values were calculated from the ratio of three and 10 times of the standard deviation of the lowest concentration in the linear range to the slope of the linear calibration plot, respectively. The relative standard deviation (RSD) was 6.6%. By considering the 250.0 mL initial and 5.0 mL final volume,

the preconcentration factor was calculated as 50.0 for Sn²⁺. The sensitivity of the ICP-OES determination of Sn²⁺ improved 47.1 times. This was calculated using the slope ratio of the linear calibration plot of the SPE-ICP-OES method in comparison to ICP-OES without the SPE method. The LOD value obtained in this study was 0.6 ng mL⁻¹ which is comparable with the values reported in the literature as follows: 1.1 and 0.7 ng mL⁻¹ for solid and liquid samples, respectively, by preconcentration on *Saccharomyces cerevisiae* and determination by ICP-OES (1), 8.4 ng mL⁻¹ by FAAS after micelle mediated extraction (14), 0.04 ng mL⁻¹ by quartz atom trap-hydride generation AAS (31), 2.86 ng mL⁻¹ by cloud point extraction before AAS measurement (2), 0.012 ng mL⁻¹ by graphite furnace AAS after cloud point extraction (4), and 1.5 ng mL⁻¹ by electrochemical hydride generation atomic fluorescence spectrometry using polyaniline-modified lead cathode (32).

The effects of possible interfering ions on the preconcentration of Sn were investigated. For this purpose, individual solutions of Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺, Cu²⁺, Ni²⁺, Co²⁺, Hg²⁺, Cd²⁺, Cr³⁺, Sb³⁺, Bi³⁺, and Al³⁺ at concentrations of 10, 100, and 1000 times higher than the concentration of Sn²⁺ were subjected to the SPE procedure. The

Fig. 3. Reusability of the same column for further preconcentration of 10.0 ng mL⁻¹ of Sn²⁺.

results show no significant decrease in the recovery of 10.0 ng mL^{-1} of Sn^{2+} , even when the concentrations of the ions were 1000 times higher than those of Sn. Additionally, a solution was prepared from the mixture of the above-mentioned ions where the concentrations were also 1000 times higher than that of Sn. The recovery value for Sn was $95.6 \pm 1.4\%$. It can be concluded that the developed method has selectivity in addition to sensitivity for Sn and could easily be applied to real samples for the determination of their Sn concentrations.

The accuracy of the method was investigated through the analysis of certified reference material NWTM-26.3 Fortified Water sample. A sample amount of 250 mL was subjected to the SPE procedure and the concentration of Sn^{2+} was found as $5.7 \pm 0.2 \text{ ng mL}^{-1}$, while it was certified as 5.9 ng mL^{-1} . Thus, it can be concluded that the method can be applied to real samples. The RSD value was found as low as 3.5%.

The developed method was also applied to real samples to determine the applicability of the method. For this purpose, three sampling points on the Tigris River were selected and the SPE method was applied to the water samples for preconcentration of Sn^{2+} . The results presented in Table VI show that the mean Sn^{2+} concentration was 10.0 ng mL^{-1} .

TABLE VI
Concentrations of Sn^{2+}
in the Water Samples
From the Tigris River

Sampling Point	Sn^{2+} (ng mL^{-1})
Heysel	10.1 ± 0.5
Ongözlü	10.0 ± 0.7
DicleKöprü	9.9 ± 0.6

Different studies have been published on the Sn concentrations in water samples and include the following: Xijun et al. (33) reported that the concentration of Sn^{2+} in a real wastewater sample was found to be $0.72 \pm 0.02 \text{ } \mu\text{g mL}^{-1}$ (33). Caldorin and Menegario (1) found the Sn^{2+} concentrations in three river water samples at 19, 18, and 40 ng mL^{-1} (1), respectively. Alp et al. (10) reported Sn^{2+} concentrations in spring and mineral water at 0.63 ± 0.03 , $1.70 \pm 0.12 \text{ ng mL}^{-1}$, respectively, determined by *in situ* trapping of stannane on a resistively heated iridium-treated tungsten coil surface. The Yuan et al. (34) study found Sn^{2+} concentrations of 0.36 and 0.12 ng mL^{-1} in sea and river water, respectively, whereas the concentration of Sn^{2+} in a tap water sample was lower than the detection limit ($\text{LOD} = 0.012 \text{ ng mL}^{-1}$).

CONCLUSION

An alternative method was developed for the preconcentration of trace levels of Sn^{2+} by solid phase extraction (SPE). *Helvella leucopus* was used as a fungal biosorbent for the preconcentration of Sn^{2+} prior to its determination by inductively coupled plasma optical emission spectrometry (ICP-OES). The important experimental parameters in the developed SPE method were optimized. Concentrations of Sn^{2+} in river water samples from Turkey were determined after the developed SPE method was applied. The sensitivity of ICP-OES was improved 47.1 times in comparison to using conventional methodology. The applicability of the method was validated by analysis of the certified reference material NWTM-26.3 Fortified Water sample with satisfactory results.

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