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ORIGINAL PAPER

Extraction of Cu^{2+} and Co^{2+} by using *Tricholoma populinum* loaded onto Amberlite XAD-4

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Abstract
In this work, an alternative preconcentration process suggested based on using *Tricholoma populinum* as a fungal biosorbent for the sensitive preconcentration of Cu^{2+} and Co^{2+}. Amberlite XAD-4 was utilized for the loading of the biomass in solid-phase extraction (SPE) procedure. It was found that *T. populinum* loaded with XAD-4 resin was a selective biosorbent for the preconcentration of Cu^{2+} and Co^{2+}. Experimental variables in SPE procedure such as pH, the flow rate of the sample, type and concentration of eluent, amount of *T. populinum* and of XAD-4 resin, sample volume, and potential interfering ion effect were studied. Surface functionalities of the metal-loaded and metal-unloaded biosorbent were determined by comparing Fourier transform infrared spectroscopy spectra and scanning electron microscopy images. Limit of detection values for Cu^{2+} and Co^{2+} were found as 0.034 and 0.019 ng mL^{-1}, respectively. The linear range was found as 0.2–15 ng mL^{-1} for both analytes. Relative standard deviation values were found as lower than 3.0%. Certified reference materials were applied for process validation, and also, the concentrations of Co^{2+} and Cu^{2+} were investigated in real water, vegetable, and soil samples. So, the method developed could be utilized for the preconcentrations of Cu^{2+} and Co^{2+} for routine analysis. This method can be used as an inexpensive and accessible alternative to GF-AAS or ICP-MS methods.

Keywords Cu · Co · Fungal biomass · Preconcentration · *Tricholoma populinum* · Validation

Introduction

The pollution of the environment (soil, water, etc.) and foods by organic and inorganic pollutants are the most important problems in today's world (Zeraatkar et al. 2016; Kilinc et al. 2013a). Among these pollutants, heavy metals have a significant influence especially on ecosystems and on human health (Jaafari and Yaghmaeian 2019) because they are non-degradable and persistent (Zeraatkar et al. 2016; Ozdemir and Kilinc 2012).

These are some conventional metal treatment approaches such as electrochemical procedures, chemical precipitation, filtration, oxidation–reduction processes, and various advanced methods of separation using membranes for heavy metal removal from the environment (Saranya et al. 2018). These conventional techniques are known as expensive and not adequate at low concentrations. The utilization of biological procedures is an alternative process for the recovery of metals from metal-polluted environments (Jaafari and Yaghmaeian 2019; Sahmoune 2018). When we compared the biological processes with the traditional treatment procedures, biological processes are known as relatively cheap, extremely effective for detoxifying even very low concentration of residues and minimizing the nonreturnable sludge level (Gong et al. 2005).

The various biological organisms such as bacteria, fungi, algae, and yeast can be employed for the uptake of toxic metals. The cell wall of these biosorbents contains a variety

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of polymers and some complex organic compounds, like cellulose, pectin, xylans, chitin, proteins, chitosan, and lipids (Mahmoud et al. 2013). These complex organic compounds and polymers are composed of various functional groups like amide, carboxylate, amine, hydroxyl, phosphate, thioether, sulfhydryl, and sulfate which can bind metal ions (Deniz and Karabulut 2017).

The non-immobilized (free) microbial cell has been used in most of the investigations for toxic metal removals. The non-immobilized biomass can be beneficial in laboratory studies, but are inconvenient for the column method because of the small particle size, mechanical resistance, and low density. High pressures can lead to free biomass disruption. In recent decades, there has been a lot of interest in the development of microbial immobilization methods (Ghaedi et al. 2006).

In solid-phase extraction (SPE) applications, the immobilized microbial cell can be employed for the recovery and the preconcentration of toxic metals at trace levels in different environmental substances. The SPE techniques have several advantages over other conventional preconcentration and separation methods, including simplicity, rapidity, high preconcentration factor, ease of automation, low consumption or non-consumption of organic solvents, and capability to join with various new methods of detection. These advantages have made SPE a very attractive method in various bio/analytical investigation fields such as biological, environmental, food, and clinical workings (Alothman et al. 2015).

In the literature, there are not enough solid-phase extraction studies that can be replaced by there are a limited number of studies regarding preconcentration from environmental samples by using fungal biomass. In this study, *T. populinum* immobilized onto Amberlite XAD-4 resins as SPE column materials were used for uptake and preconcentration of Cu^{2+} and Co^{2+}. For this respect, different parameters such as the effect of pH value, sample flow rate, amounts of Amberlite XAD-4 and biosorbent, eluent type and volume, foreign ions, sample volume, and column reuse were studied.

Materials and methods

Instrumentation

The levels of Cu^{2+} and Co^{2+} were determined by employing a PerkinElmer Optima 2100 DV (PerkinElmer, Inc., Shelton, CT, USA) inductively coupled plasma optical emission spectrometry (ICP-OES) at 327,393 nm for Cu and 228,616 nm for Co. The pH meter Mettler Toledo MPC 227 (Polaris Parkway, Columbus, OH, USA) was used for the pH measurements. SPE analyses were conducted using filtration columns (1.0/10.0 cm), equipped with polypropylene frites. Peristaltic pump (Watson-Marlow 323, Milford, MA, USA) was employed for the control of the standard and sample solutions flow rates to desired flow rates.

Reagents and solutions

Stock solutions (1000 µg mL^{-1}) of Cu^{2+} and Co^{2+} were utilized through dilution to prepare work standards. All chemicals utilized were of high purity and reagent grade unless stated otherwise. Distilled water (doubly) was utilized during all SPE studies. When not in use, laboratory glassware was permanently kept in 1.0 mol L^{-1} nitric acid. Concentrated hydrochloric acid (36.5–38.0%), hydrogen peroxide (35%), and nitric acid (65%) were obtained from (Sigma-Aldrich, Germany). The developed method was validated for the Cu and Co through the analysis of DORM-2 (dogfish muscle certified reference material for trace elements), NWTM-15 (certified samples of fortified water), 1643e (standard reference material for trace elements in water), NCSZC 73014 (powdered tea) which were obtained from National Research Council of Canada-NRC-CNRC, High Purity Standard, National Institute of Standard and Technology, China National Analysis Center for Iron and Steel, respectively. Amberlite XAD-4 (polystyrene divinylbenzene) was supplied from Sigma-Aldrich Co., USA.

Preparation of fungal biomass

Tricholoma populinum, collected from Siirt, Turkey, was used as the biosorbent in this investigation. It was subjected to a procedure before using for preconcentration (Kilinc et al. 2013a). Briefly, it was cleaned two times with distilled water in order to eliminate and finally dried at 25 °C. Dried *T. populinum* was ground to obtain fine powder in a porcelain mortar. It was then dried in the oven at 120 °C for 2 h to obtain dead cells. To control the death of cells, dried cells were inoculated into malt agar at 25 °C for 25 h. No growth was observed when the cells died completely.

Preparation of the column

A 0.25 g of dried fungal biomass powder was blended with 1 g XAD-4 resins for 24 h. The quantities of *T. populinum* taken up by XAD-4 resins were checked by measuring the rise in resin weight in the wake of blending the paste which was warmed in an oven for 60 min at 105 °C to dry. Repeated steps of wetting and drying were carried out to maximize the contact among *T. populinum* and resin XAD-4, in order to increase the yield of immobilization. At last, immobilized *T. populinum* was grounded to get the size of 20–60 mesh and packed into a column of SPE (1.0 cm × 10.0 cm).

General sorption studies

Before optimization of the preconcentration method, fungal biomass-loaded XAD-4 was tried as a potential resin for the preconcentration of different metal cations for evaluating the selectivity and/or specificity. For this purpose, 50 mL of the solution includes a mixture of metal cations at the concentrations of 20.0 ng mL^{-1} of Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Cr^{6+}, Pb^{2+}, and As^{3+}, and a solution pH of 3.0, 6.0, and 9.0 was adjusted by adding the required NH_3 and HCl quantities. The model metal solutions were transferred to the bio-SPE column at a 1.0 mL/min flow rate using a peristaltic pump. The distilled water of 10.0 mL was then transferred to the column of the bio-SPE, and a 5.0 mL HCl (1.0 mol L^{-1}) was then eluted to the remaining metal cations. The concentrations of metal cations were determined by ICP-OES. So, the results were assessed and decided to standardize the method to the element(s) that had an affinity to the resin loaded with the fungus. All of the experiments were performed at least three times.

Loading capacity

Loading capacity of the *T. populinum*-loaded Amberlite XAD-4 was determined for Cu^{2+} and Co^{2+}, since adsorption and elution ability of Cu^{2+} and Co^{2+} were higher than those of other metal cations. For this purpose, the batch equilibrium method was applied. In this method, Erlenmeyer flask (250.0-mL) containing 50.0 mL of the Cu^{2+} and Co^{2+} at the concentrations of 50.0 mg L^{-1} was used at optimum pH values for Cu^{2+} and Co^{2+} cations. The 100.0 mg dried powdered dead cells was added to metal solutions for 120 min at 25 °C on a Julaba SW72 shaker (Seelbach, Germany) at 120 rpm. These cells were then separated for 10 min at 10,000 rpm by centrifugation.

The supernatant and pellet (after HNO_3 digestion) were analyzed to determine the amount of residual metal by ICP-OES. The concentration of biosorbed Cu^{2+} and Co^{2+} ions was determined by employing the equation shown in our previous study (Kilinc et al. 2013a).

Sample preparation

Samples were bought from local markets and washed in fresh tap water to remove any foreign objects, and then cleaned again with deionized water. They were dried in an oven at 80 °C for 24 h. 1.0 g of powdered sample was added to 5.0 mL HNO_3:HCl (v/v) and warmed on a hot plate. After drying 6.0 mL of HNO_3:HCl:H_2O_2 (1:1:0.2 v/v/v) was added. This solution was placed in the Berghof MWS3 microwave oven (Berghof, Tubingen, Germany) and was heated by microwave irradiation up to 170 °C and kept for 5.0 min; subsequently, the temperature was brought to 200 °C in 15 min and then kept for 1.0 min; finally, the temperature was reduced to 100 °C, waiting for 20 min. The final volume was adjusted to 50 and/or 100.0 mL volume after digestion, and the pH was calibrated before the bio-SPE method to the appropriate level. The amounts of the tested metal ions in the samples were measured by ICP-OES. A 100 mL of NWTM-15 and 1643e was directly added to the developed process after adjusting pH. A 1.0-g portion of DORM-2 and ZC73014 was digested applying the same procedure indicated for the real substances.

Results and discussion

Specificity/selectivity of biosorbent

By considering the complex and rich surface functionality of fungus-loaded resin, preliminary SPE studies were studied for a 50 mL mixture of metal cations at the concentrations of 20.0 ng mL^{-1} of Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Cr^{6+}, Pb^{2+}, and As^{3+}. High elution recovery values (> 95%) were achieved at pH 6.0 than other values. According to the results, quantitative adsorption and elution values were reached for Cu^{2+} and Co^{2+}. The elution recoveries for other cations were not satisfactory. Further experiments were focused on the optimization of the SPE method only for Cu^{2+} and Co^{2+}.

Surface studies

FT-IR was utilized to study the surface functional structure of *T. populinum* and to understand the complexation with targeted metal ions. The broad peaks on 3370 cm^{-1}, 2920 cm^{-1}, 1630–1550 cm^{-1}, 1380 cm^{-1}, 1020 cm^{-1}, and 900 cm^{-1} were corresponding to alcohol –OH stretching, carboxylic acid –OH stretching, NH bending, S=O stretching of a sulfate group, S=O stretching of sulfoxide, and C-N stretching of aromatic amine, respectively (Fig. 1a). After immobilization with Amberlite XAD-4, different peaks were observed at 650–1000 cm^{-1} from resin (Fig. 1b). Figure 1c, d shows that the peak on 1380 cm^{-1} shifted to 1340 cm^{-1} this could be attributed to the bond of Cu^{2+} and Co^{2+} with amino groups. Additionally, it could be discussed from the HSAB (hard and soft acid and bases) theory that Cu^{2+} and Co^{2+} are borderline cations and they have an affinity to functional groups that contain amine and sulfur.

SEM imaging gives information on surface macrostructure. The SEM images presented in Fig. 2a–e show that the developed biosorbent has a homogeneous structure. From our previous experiences, we want to highlight that it is very important because of the reusability of the same SPE column for further usage.

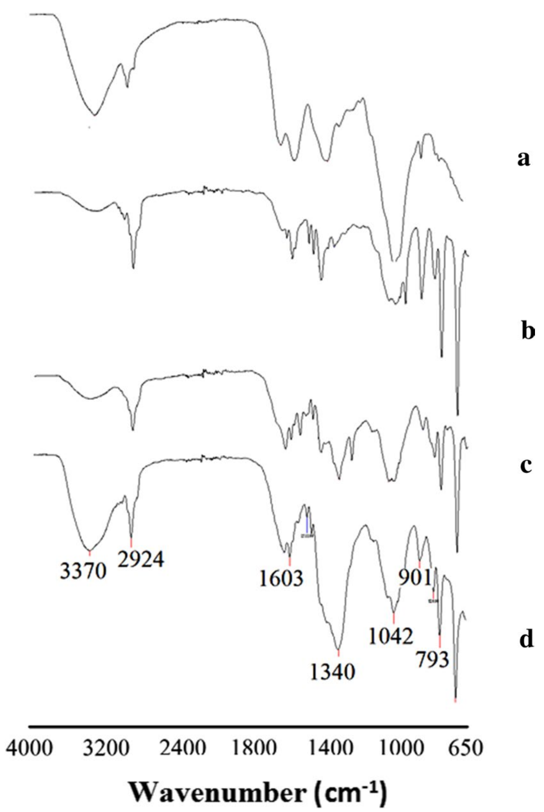

Fig. 1 FT-IR spectra of **a** *T. populinum*, **b** *T. populinum*-loaded Amberlite XAD-4, **c** Cu^{2+} on *T. populinum*-loaded Amberlite XAD-4, **d** Co^{2+} on *T. populinum*-loaded Amberlite XAD-4

pH effect

It has been already indicated that pH is a significant parameter in biosorption performance by various microorganisms (Ozdemir et al. 2013a). The effect of pH on the recovery of Cu^{2+} and Co^{2+} was tested on the pH values ranging from 2.0 to 8.0 by using *T. populinum* loaded onto Amberlite XAD-4. The results are shown in Fig. 3.

The optimal pH was determined as pH 5.0 and 6.0 for Co^{2+} and Cu^{2+}, respectively. At the pH ranges of 7.0 and 8.0, the percentage of biosorbed metal of immobilized *T. populinum* was found as 98.4% and 97.6% for Co^{2+} and 98.8% and 96.5% for Cu^{2+}, while it was 59.7% and 89.4% for Co^{2+} and 51.4% and 81.3% for Cu^{2+} at the range of 3.0 and 4.0, respectively. The metal biosorption reduces at low pH ranges due to competition for binding sites of biosorbent cell wall among cations and the products of acid hydrolysis, while the heavy metals demonstrate a tendency to precipitate leading to lower biosorption at higher pH ranges (Ozdemir et al. 2013b; Hoque et al. 2015). The values of pH 5.0 and 6.0 were used for the following studies in order to recover Co^{2+} and Cu^{2+}, respectively.

Sample flow rate effect

The sample solution flow rate has a significant effect due to the interaction of analytes with the biomass (Duran et al. 2009). The flow rate effect of sample solution on retentions of Cu^{2+} and Co^{2+} is presented in Fig. 4. The recoveries of Cu^{2+} and Co^{2+} were not importantly changed up to a flow rate of 3 mL/min. Quantitative retentions were obtained when the flow rate was between the ranges of 1–3 mL/min. As expected, at the lower flow rates of the sample solution, there were more interaction times between metal ions and biosorbent binding sites, so higher metal recovery occurred on biosorbent binding cites. The retentions of Cu^{2+} and Co^{2+} decreased with increasing the flow rate of 3 mL/min. When the flow rate was raised from 3 to 5 mL/min, the recoveries of Cu^{2+} and Co^{2+} were decreased from 98.6–90.2 to 98.3–88.1%, respectively. Therefore, the flow rate of 3.0 mL/min was used for all further studies.

Effect of amounts of Amberlite XAD-4

The influence of the quantities of solid-phase extraction matrix on recoveries of Cu^{2+} and Co^{2+} was tested by using Amberlite XAD-4. The results are presented in Fig. 5. The recovery values raised when the amounts of Amberlite XAD-4 were raised until 800 mg. It was found that recovery rates of Cu^{2+} and Co^{2+} were 87.9% and 85.6%, respectively, when the amounts of resin were 500 mg. The recoveries were 100% for Cu^{2+} and Co^{2+}, whereas the amount of Amberlite XAD-4 was 800 mg. The percentage of recoveries of Co^{2+} and Cu^{2+} did not change above 800 mg. From that point of view, 800 mg of resin was utilized for the following solid-phase extraction parameters.

Effect of biosorbent amount

In solid phase extraction studies, the amount of biosorbent affects the efficiency of the immobilized biosorbent on a solid matrix. It is obvious that the factor of biosorbent amounts plays a significant role in SPE studies. From that point of view, to obtain a higher recovery yield, the optimum amount of biosorbent must be determined. Various doses of biosorbent 100, 150, 200, 250, 300, 350, and 400 mg were tested. The influence of biosorbent amount on recoveries of Cu^{2+} and Co^{2+} is presented in Fig. 6. The recoveries of Cu^{2+} and Co^{2+} raised up until 250 mg. The recoveries' value did not change up to 400 mg. It was observed that there was a slight decrease in recovery with rising up of biomass dose. As a result, it can be indicated that the reduction in recovery with the rise in biomass amount can be explained by considering the saturation of biomass surface and the cell aggregation (Okumus et al. 2015).

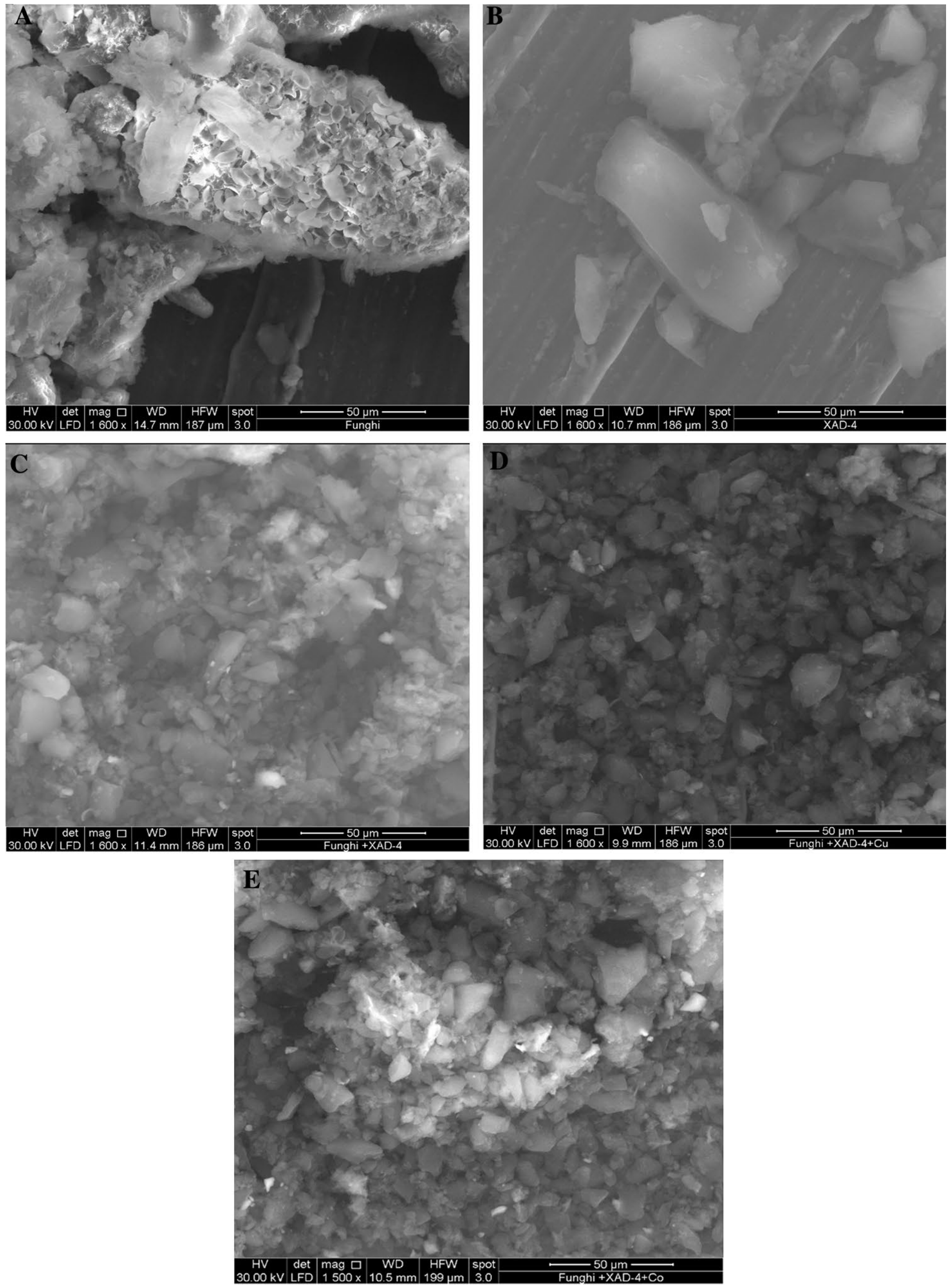

Fig. 2 SEM images of **a** *T. populinum*, **b** Amberlite XAD-4, **c** *T. populinum* onto Amberlite XAD-4, **d** Cu^{2+} on *T. populinum*-loaded Amberlite XAD-4, **e** Co^{2+} on *T. populinum*-loaded Amberlite XAD-4

Eluent type and volume effect

Different amounts of hydrochloric acid (HCl) and nitric acid (HNO_3) were used for the desorption of Cu^{2+} and Co^{2+} from immobilized *T. populinum* onto Amberlite resin. Table 1 shows the recovery percentages of Co^{2+} and Cu^{2+}. The desorption tests revealed the possibility to reuse the biosorbent for further metal ion recoveries. In addition, desorption solutions cannot destroy the biosorbent surface area (Marahel et al. 2009; Ziaei et al. 2014).

It could be obviously shown that 1 M HCl and HNO_3 were adequate for quantitative elution (> 95%). The influence of HCl and HNO_3 volume (3 and 5 mL) on the retentions of Cu^{2+} and Co^{2+} was experimented by using 0.5 and 1 M HCl and HNO_3. The maximum recoveries were obtained with 5 mL of 1 M HCl for Cu^{2+} and Co^{2+}. Therefore, 5 mL of HCl (1 M) was utilized as eluent in all following studies.

Sample volume effect

The sample volume is a major parameter in solid-phase extraction works using real samples to achieve high preconcentration factors. The most suitable sample volume must be studied to use real samples including very low

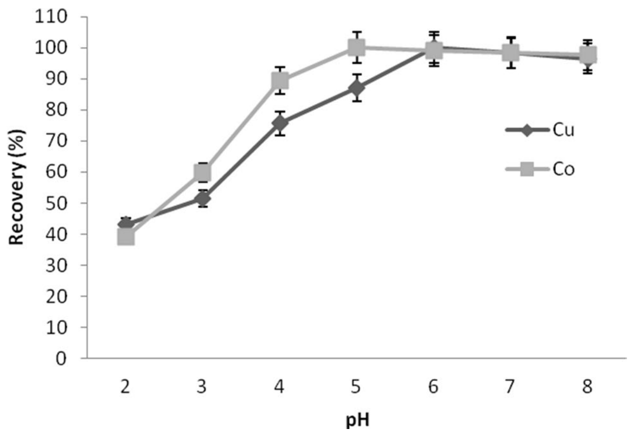

Fig. 3 Effect of pH on the recoveries 50 mL of 20.0 ng mL^{-1} of Cu^{2+} and Co^{2+} (elution at 1.0 mL min^{-1} flow rate by 5.0 mL 1.0 M HCl; 200 mg of *T. populinum* loaded on 1000 mg of Amberlite XAD-4)

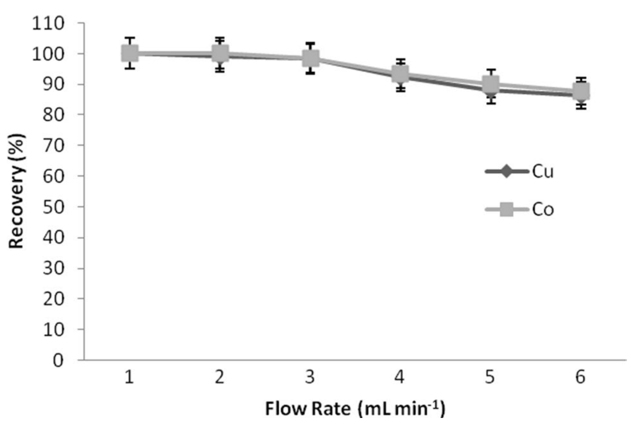

Fig. 4 Effect of the flow rate of the initial solution on biosorption of Cu^{2+} and Co^{2+}

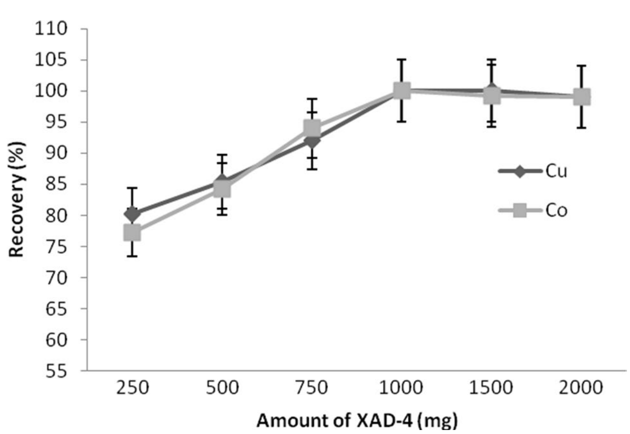

Fig. 5 Effect of amounts of Amberlite XAD-4 on the recoveries 50 mL of 20.0 ng mL^{-1} of Cu^{2+} and Co^{2+} (pH 6.0; elution at 3.0 mL min^{-1} flow rate by 5.0 mL 1.0 M HCl)

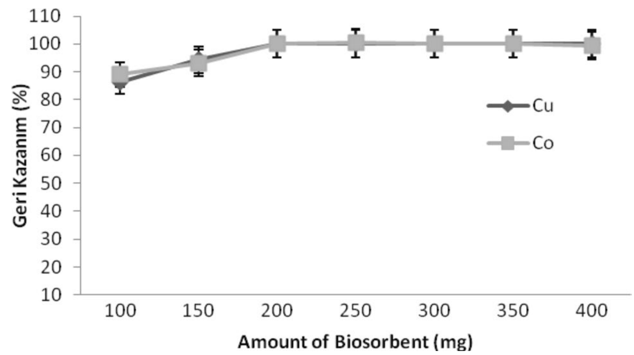

Fig. 6 Effect of amounts of *Tricholoma populinum* on the recoveries 50 mL of 20.0 ng mL^{-1} of Cu^{2+} and Co^{2+} (pH 6.0; elution at 3.0 mL min^{-1} flow rate by 5.0 mL 1.0 M HCl)

Table 1 Eluent type and volume effect

Eluent type	Volume (mL)	Concentration (mol L^{-1})	Recovery (%)	
			Cu^{2+}	Co^{2+}
HCl	3	0.5	92.3 ± 0.2	91.4 ± 0.3
	5	0.5	96.2 ± 0.4	95.9 ± 0.1
	3	1	95.4 ± 0.3	94.3 ± 0.5
	5	1	99.8 ± 0.2	99.7 ± 0.4
HNO_3	3	0.5	87.5 ± 0.6	86.9 ± 0.2
	5	0.5	95.7 ± 0.5	94.8 ± 0.6
	3	1	92.7 ± 0.2	91.6 ± 0.4
	5	1	97.9 ± 0.3	97.4 ± 0.5

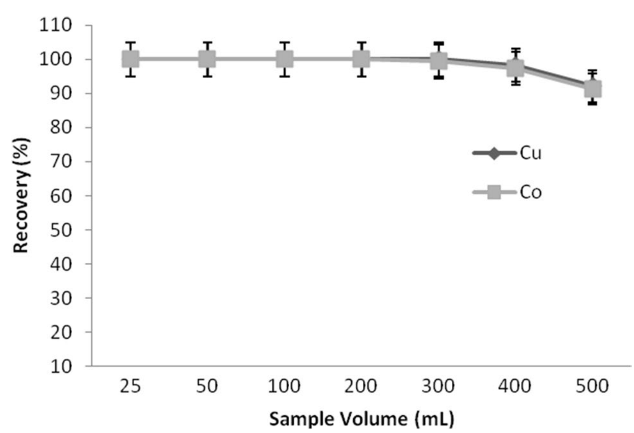

Fig. 7 Effect of sample volume on the recovery of Co^{2+} and Cu^{2+}

concentrations of metal ions, trace metal ions or radionuclides (Kilinc et al. 2013b). For these reasons, the sample volume effect on the retentions of Cu^{2+} and Co^{2+} was examined under the optimum conditions. The results obtained are shown in Fig. 7.

The quantitative retentions of Cu^{2+} and Co^{2+} were obtained when the sample volume was up to 500 mL. The recoveries of tested metal ions reduced at higher sample volumes. The recovery rate of 500 mL sample volume was found as 98.9% and 99.2% for Cu^{2+} and Co^{2+}, respectively. So, the preconcentration factor of 100 was obtained for a desorption volume of 5.0 mL and a sample volume of 500 mL.

Effect of foreign ions

It was reported that a high concentration of foreign ions could be caused by matrix effects in the spectroscopic determination of analytes in natural samples (Kilinc et al. 2013a). The interfering ion effect on the uptake of Cu^{2+} and Co^{2+} was tested by passing 50 mL of binary solution at concentrations of 0.1 µg/mL Cu^{2+} and Co^{2+} through the immobilized *T. populinum* SPE microcolumn. As presented in Table 2, the results showed that 5000 mg/L (50,000-fold) K^{+} and Na^{+}, 100 mg/L (1000-fold) Ca^{2+}, 50 mg/L (500-fold) Mg^{2+} and Mn^{2+}, 10 mg/L (100-fold) Cu^{2+}, Fe^{2+}, and Zn^{2+}, and 5 mg/L (50-fold) Cd^{2+} and Pb^{2+} did not have significant influence on the recovery and determination of Co^{2+} and Cu^{2+}. As a result, it can be indicated that the immobilized *T. populinum* microcolumn has a perfect selectivity for the biosorption of Cu^{2+} and Co^{2+} under the optimum conditions.

The effect of column reuse

The repeatability of biomass immobilized SPE microcolumn is very important for bioanalytical and biotechnological perspectives (Oral et al. 2015). The results obtained are shown in Fig. 8. It was found that *T. populinum*-loaded SPE column can be reused many times without a significant reduction in the recovery of analytes. After 20 times of biosorption and desorption studies, the quantitative recoveries were obtained with tested metals when *T. populinum* immobilized on XAD-4 resin was applied as a biosorbent.

Table 2 Effect of foreign ions

Interference	Interference-to-metal ion ratio	Recovery (%)[a]	
		Co^{2+}	Cu^{2+}
Na^{+}	5000	97.0 ± 1.9	95.8 ± 2.8
K^{+}	5000	97.7 ± 2.1	98.3 ± 1.1
Ca^{2+}	100	99.2 ± 0.3	99.0 ± 0.5
Mg^{2+}	50	98.1 ± 1.4	98.9 ± 0.4
Mn^{2+}	50	99.1 ± 0.5	99.0 ± 0.3
Cu^{2+}	10	99.1 ± 0.2	99.5 ± 0.1
Zn^{2+}	10	99.5 ± 0.3	99.5 ± 0.2
Fe^{2+}	10	98.2 ± 1.3	98.5 ± 1.2
Cd^{2+}	5	98.4 ± 1.1	99.1 ± 0.5
Pb^{2+}	5	99.6 ± 0.1	97.9 ± 1.7

[a]Concentration of the metal ions is 0.1 µg/mL

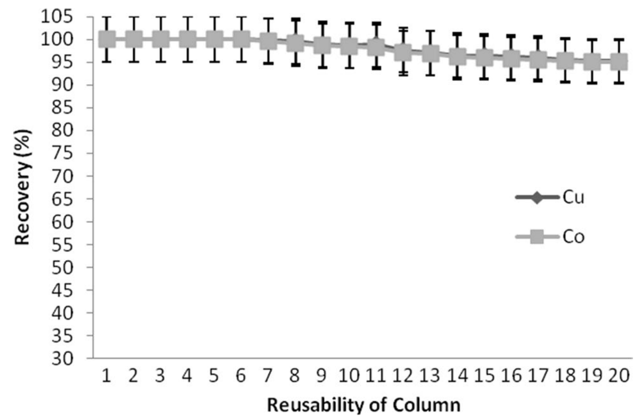

Fig. 8 Effect of the reuse of the column

Analytical characteristics

Analytical characteristics of the developed bio-SPE method for the preconcentrations of Cu^{2+} and Co^{2+} were expressed in view of LOQ (limit of quantification), LOD, RSD, linearity, correlation coefficient, and preconcentration factor. The LOD values were calculated as 0.034 ng mL^{-1} for Cu^{2+} and 0.019 ng mL^{-1} for Co^{2+}, while LOQ values were calculated as 0.11 ng mL^{-1} for Cu^{2+} and 0.065 ng mL^{-1} for Co^{2+}. The linear range was 0.2–15 ng mL^{-1} for both analytes with correlation coefficients were higher than 0.9900 (Table 3). When considering the amount of 500 mL of sample and 5.0 mL of desorption, the preconcentration factor was obtained as 100. Maximum adsorption capacities were found from batch experiments as 28.7 and 30.3 mg kg^{-1}, respectively, for Cu^{2+} and Co^{2+}.

The accuracy of the developed method was controlled by performing to certified and/or standard reference materials before application to real samples. The liquid samples were applied to the developed method after pH adjustment, whereas solid samples were digested in the microwave oven before the application of the method. The results are presented in Table 4. It is to be noted that the results obtained were in agreement with the certified values.

Taking into consideration the methods developed for Cu^{2+} and Co^{2+} preconcentrations on the literatures, we

Table 3 Analytical characteristics of the method

Parameter	Cu^{2+}	Co^{2+}
LOD (ng mL^{-1})	0.034	0.019
LOQ (ng mL^{-1})	0.11	0.63
Linear range (ng mL^{-1})	0.2–15	0.2–15
r^2	0.9991	0.9992
RSD (%)	2.4	2.8
Preconcentration factor	100	100

Table 4 Application of the method to certified reference samples

Reference sample	Certified		Found	
	Cu	Co	Cu	Co
DORM-2	2.34 ± 0.16[a]	0.182 ± 0.031[a]	2.29 ± 0.15[a]	0.179 ± 0.04[a]
ZC73014	18.6 ± 0.7[a]	0.22 ± 0.02[a]	18.0 ± 0.8[a]	0.21 ± 0.02[a]
NWTM-15	18.3[b]	15.1[b]	18.1 ± 0.8[b]	15.0 ± 0.5[b]
1643e	22.76 ± 0.31[b]	27.06 ± 0.32[b]	22.12 ± 0.67[b]	26.86 ± 0.70[b]

[a]μg/g

[b]ng/mL

Table 5 Comparison of analytical characteristics of the developed method with the literature

Metal Ions	Sorbent	Detection limit (LOD) (mg L_1)	PF[a]	Samples	References
Cd Co Cu Ni	Amberlite XAD-2 resin functionalized with pyrocatecho	Cd: 0.31 Co: 0.32 Cu: 0.39 Ni: 1.64	Cd: 39 Co: 69 Cu: 36 Ni: 41	Food samples	Lemos et al. (2006a)
Ni Co Hg	Multiwalled carbon nanotubes chelating with sodium diethyldithiocarbamate	Ni: 0.04 Co: 0.05 Hg: 0.9	Ni: 200 Co: 200 Hg: 200	Water samples	Zhou et al. (2014)
Cu	Chitosan biopolymer modified with 5-sulfonic acid 8-hydroxyquinoline	Cu: 0.3	19.1	Water samples	Martins et al. (2004)
Cu Cd Co Ni Pb	6-(2-Thienyl)-2-pyridine carboxaldehyde-functionalized Amberlite XAD-4	Cu: 0.39 Cd: 0.14 Co: 0.88 Ni: 0.82 Pb: 2.54	Cu: 31.5 Cd: 28.1 Co: 23.7 Ni: 20 Pb: 30.3	Water samples	Karadas and Kara (2013a)
Co	1-(2-Pyridylazo) 2-naphthol (PAN)	Co: 0.03	Co: 101	Rice and water	Jiang et al. (2008)
Cu Cd Co Pb Mn	Amberlite XAD-4 functionalized with 2,6-pyridinedicarboxaldehyde	Cu: 0.29 Cd: 0.13 Co: 0.58 Mn: 0.23 Pb: 2.19	Cu: 27.3 Cd: 27.6 Co: 23.6 Mn: 28.9 Pb: 27.9	Water samples,	Karadas and Kara (2013b)
Cu Cd Mn Co Ni Pb	Amberlite XAD-4 modified with 8-hydroxy-2-quinoline carboxaldehyde	Cu: 0.35 Cd: 0.14 Mn: 0.2 Co: 0.70 Ni: 0.72 Pb: 2.92	Cu: 22.3 Cd: 27.6 Mn: 24.7 Co: 23.2 Ni: 20.2 Pb: 24.1	Water samples	Karadas et al. (2013)
Co	Chromosorb 105	Co: 2.5	Co: 50	Tap water and table salt samples	Karatepe et al. (2002)
Pb Co	Silica-coated magnetic multiwalled carbon nanotubes impregnated with 1-(2-pyridylazo)-2-naphthol	Pb: 1.76 Co: 0.55	Pb: 15 Co: 15	Water samples	Khan et al. (2016)
Co Cu Ni	Amberlite XAD-2 functionalized with 2-[20-(6-methyl-benzothiazolylazo)]-	Co: 0.34 Cu: 0.87 Ni: 0.81	Co: 30 Cu: 30 Ni: 24	Food samples	Lemos et al. (2006b)
Co Cu	*Tricholoma populinum* loaded onto Amberlite XAD-4	Co: 0.019 Ni: 0.034	Co: 100 Ni: 100	Food and water samples	This study

[a]Preconcentration factor

Table 6 Implementation of the method to actual samples

Sample	Cu	Co
Tigris River water, Diyarbakır	6.9 ± 0.2[a]	3.4 ± 0.2[a]
Tap water	< LOD	< LOD
Potatoes	6.5 ± 0.4[b]	8.0 ± 0.5[b]
Purslane	86.5 ± 4.6[c]	26.9 ± 1.1[c]
Okra	50.4 ± 2.1[c]	123 ± 5.6[c]
Onion	10.1 ± 0.5[b]	13.2 ± 0.6[b]
Aubergine	25.0 ± 1.4[b]	35.5 ± 2.7[b]
Spinach	< LOD	26.0 ± 1.9[b]
Parsley	16.5 ± 1.1[b]	30.1 ± 2.0[b]
Mint	20.7 ± 1.9[b]	< LOD
Tomato	9.9 ± 0.7[b]	22.1 ± 0.8[b]
Cucumber	30.2 ± 2.4[b]	10.9 ± 0.4[b]
Carrot	5.0 ± 0.4[b]	8.1 ± 0.6[b]
Black tea	9.4 ± 0.6[b]	0.8 ± 0.01[b]

[a]ng/mL
[b]μg/g
[c]ng/g

should highlight the over features of our method. Comparative information is presented in Table 5. We could clearly highlight that the achieved preconcentration factors were satisfactory for ultra-trace detection.

Importantly, LOD values were reached as lower as eliminate the use of ICP-MS and/or GF-AAS. Thus, the developed method could be applied to real sample analysis. Cu^{2+} and Co^{2+} concentrations in real samples such as Tigris River water, tap water, potatoes, purslane, okra, onion, aubergine, spinach, parsley, mint, tomato, cucumber, carrot, and black tea were measured by ICP-OES (Table 6).

Conclusion

An alternative method of preconcentration based on the use of *T. populinum* immobilized on Amberlite XAD-4 as a biosorbent was developed for Cu^{2+} and Co^{2+}. The significant experimental parameters were studied in detail to find the optimum values. The optimal pH was determined as pH 5.0 and 6.0 for Co^{2+} and Cu^{2+}, respectively, and also, the flow rate of 3.0 mL/min and 5 mL of HCl (1 M) was utilized as flow rate and elution solution, respectively. The preconcentration factor was found as 100. 800 mg of resin and 200 mg of *T. populinum* were utilized as optimum amounts. The effect of possible interfering ions was also examined. The developed method was validated by the certified reference sample analysis. Applicability of the method was shown by also applying to real samples. By considering the 100 times preconcentration factor, it is envisaged that the recommended SPE method could find application in the routine analysis of Cu^{2+} and Co^{2+} at ultra-trace levels in the absence of ICP-MS and GF-AAS.

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References

Alothman ZA, Yilmaz E, Habila M, Soylak M (2015) Solid phase extraction of metal ions in environmental samples on 1-(2-pyridylazo)-2-naphtholim pregnated activated carbon cloth. Ecotoxicol Environ Saf 112:74–79. https://doi.org/10.1016/j.ecoenv.2014.10.032

Deniz F, Karabulut A (2017) Biosorption of heavy metal ions by chemically modified biomass of coastal seaweed community: studies on phycoremediation system modeling and design. Ecol Eng 106:101–108. https://doi.org/10.1016/j.ecoleng.2017.05.024

Duran A, Tuzen M, Soylak M (2009) Preconcentration of some trace elements via using multiwalled carbon nanotubes as solid phase extraction adsorbent. J Hazard Mater 169:466–471. https://doi.org/10.1016/j.jhazmat.2009.03.119

Ghaedi M, Fathi MR, Shokrollahi A, Shajarat F (2006) Highly selective and sensitive preconcentration of mercury ion and determination by cold vapor atomic absorption spectroscopy. Anal Lett 39:1171–1185. https://doi.org/10.1080/00032710600622167

Gong R, Ding Y, Liu H, Chen Q, Liu Z (2005) Lead biosorption and desorption by intact and pretreated *Spirulina maxima* biomass. Chemosphere 58:125–130. https://doi.org/10.1016/j.chemosphere.2004.08.055

Hoque Md, Ikram Ul, Chowdhury DA, Holze R, Chowdhury AN, Azam MdS (2015) Modification of Amberlite XAD-4 resin with 1,8-diaminonaphthalene for solid phase extraction of copper, cadmium and lead, and its application to determination of these metals in dairy cow's milk. J Environ Chem Eng 3:831–842. https://doi.org/10.1016/j.jece.2015.03.020

Jaafari J, Yaghmaeian K (2019) Optimization of heavy metal biosorption onto freshwater algae (*Chlorella coloniales*) using response surface methodology (RSM). Chemosphere 217:447–455. https://doi.org/10.1016/j.chemosphere.2018.10.205

Jiang H, Qin Y, Hu B (2008) Dispersive liquid phase microextraction (DLPME) combined with graphite furnace atomic absorption spectrometry (GFAAS) for determination of trace Co and Ni in environmental water and rice samples. Talanta 74:1160–1165. https://doi.org/10.1016/j.talanta.2007.08.022

Karadas C, Kara D (2013a) Online preconcentration system using 6-(2-thienyl)-2- pyridine carboxaldehyde functionalized Amberlite XAD-4 resin for the determination of trace elements in waters by flame atomic absorption spectrometry. J AOAC Int 96:642–649. https://doi.org/10.5740/jaoacint.12-091

Karadas C, Kara D (2013b) On-line preconcentration and determination of trace elements in waters and reference cereal materials by flow injection—FAAS using newly synthesized 8-hydroxy-2-quinoline carboxaldehyde functionalized Amberlite XAD-4. J Food Compos Anal 32:90–98. https://doi.org/10.1016/j.jfca.2013.07.003

Karadas C, Turhan O, Kara D (2013) Synthesis and application of a new functionalized resin for use in an on-line, solid phase extraction system for the determination of trace elements in waters and reference cereal materials by flame atomic absorption spectrometry. Food Chem 141:655–661. https://doi.org/10.1016/j.foodchem.2013.03.042

Karatepe A, Soylak M, Elci L (2002) Cobalt determination in natural water and table salt samples by flame atomic absorption spectroscopy/on-line solid phase extraction combination. Anal Lett 35:2363–2374. https://doi.org/10.1081/AL-120016109

Khan M, Yilmaz E, Soylak M (2016) Vortex assisted magnetic solid phase extraction of lead(II) and cobalt(II) on silica coated magnetic multiwalled carbon nanotubes impregnated with 1-(2-pyridylazo)-2-naphthol. J Mol Liq 224:639–647. https://doi.org/10.1016/j.molliq.2016.10.023

Kilinc E, Dundar A, Ozdemir S, Okumus V (2013a) Solid phase extraction based on the use of *Agaricus arvensis* as a fungal biomass for the preconcentrations of Pb and Al prior to their determination in vegetables by ICP-OES. At Spectrosc 34:78–88

Kilinc E, Dundar A, Ozdemir S, Okumus V (2013b) 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. At Spectrosc 34:133–137

Lemos VA, da Silva DG, de Carvalho AL, de Andrade Santana D, dos Santos Novaes G, dos Passos AS (2006a) Synthesis of Amberlite XAD-2-PC resin for preconcentration and determination of trace elements in food samples by flame atomic absorption spectrometry. Microchem J 84:14–21. https://doi.org/10.1016/j.microc.2006.03.006

Lemos VA, David GT, Santos LN (2006b) Synthesis and application of XAD-2/Me-BTAP resin for on-line solid phase extraction and determination of trace metals in biological samples by FAAS. J Braz Chem Soc 17:697–704. https://doi.org/10.1590/S0103-50532006000400010

Mahmoud ME, Yakout AA, Abdel-Aal H, Osman MM (2013) Immobilization of *Fusarium verticillioides* fungus on nano-silica (NSi–Fus): a novel and efficient biosorbent for water treatment and solid phase extraction of Mg(II) and Ca(II). Biores Technol 134:324–330. https://doi.org/10.1016/j.biortech.2013.01.171

Marahel F, Ghaedi M, Shokrollahi A, Montazerozohori M, Davoodi S (2009) Sodium dodecyl sulfate coated poly (vinyl) chloride: an alternative support for solid phase extraction of some transition and heavy metals. Chemosphere 74:583–589. https://doi.org/10.1016/j.chemosphere.2008.09.034

Martins AO, da Silva EL, Carasek E, Laranjeira MCM, de Favere VT (2004) Sulphoxine immobilized onto chitosan microspheres by spray drying: application for metal ions preconcentration by flow injection analysis. Talanta 63:397–403. https://doi.org/10.1016/j.talanta.2003.11.011

Okumus V, Çelik KS, Özdemir S, Dündar A, Kılınç E (2015) Biosorptions of chlorophenoxy acid herbicides from aqueous solution by using low-cost agricultural wastes. Desalin Water Treat 56:1898–1907. https://doi.org/10.1080/19443994.2014.961562

Oral EV, Ozdemir S, Dolak I, Okumus V, Dundar A, Ziyadanoğulları B, Aksoy Z, Onat R (2015) *Anoxybacillus* sp. SO B1 immobilized Amberlite XAD-16 for solid phase preconcentration of Cu(II), Pb(II) and their determinations by flame atomic absorption spectrometry. Bioremediat J 19:139–150. https://doi.org/10.1080/10889868.2014.978837

Ozdemir S, Kilinc E (2012) *Geobacillus thermoleovorans* immobilized on Amberlite XAD-4 resin as a sorbent for solid phase extraction of uranium (VI) prior to its spectrophotometric determination. Microchim Acta 178:389–397. https://doi.org/10.1007/s00604-012-0841-2

Ozdemir S, Kilinc E, Poli A, Nicolaus B (2013a) Resistance and Bioaccumulation of Cd^{2+}, Cu^{2+}, Co^{2+} and Mn^{2+} by thermophilic bacteria, *Geobacillus thermantarticus* and *Anoxybacillus amylolyticus*. Ann Microbiol 63:1379–1385. https://doi.org/10.1007/s13213-013-0598-9

Ozdemir S, Kilinc E, Poli A, Nicolaus B (2013b) Biosorption of heavy metals (Cd^{2+}, Cu^{2+}, Co^{2+} and Mn^{2+}) by thermophilic bacteria, Geobacillus thermantarcticus and Anoxybacillus amylolyticus: equilibrium and kinetic studies. Bioremediat J 17:86–96. https://doi.org/10.1080/10889868.2012.751961

Sahmoune MN (2018) Performance of *Streptomyces rimosus* biomass in biosorption of heavy metals from aqueous solutions. Microchem J 141:87–95. https://doi.org/10.1016/j.microc.2018.05.009

Saranya K, Sundaramanickam A, Shekhar S, Meena M, Sathishkumar RS, Balasubramanian T (2018) Biosorption of multi-heavy metals by coral associated phosphate solubilising bacteria *Cronobacter muytjensii* KSCAS2. J Environ Manag 222:396–401. https://doi.org/10.1016/j.jenvman.2018.05.083

Zeraatkar AK, Ahmadzadeh H, Talebi AF, Moheimani NR, McHenry MP (2016) Potential use of algae for heavy metal bioremediation, a critical review. J Environ Manag 181:817–831. https://doi.org/10.1016/j.jenvman.2016.06.059

Zhou Q, Xing A, Zhao K (2014) Simultaneous determination of nickel, cobalt and mercury ions inwater samples by solid phase extraction using multiwalled carbon nanotubes as adsorbent after chelating with sodiumdiethyldithio carbamate prior to high performance liquid chromatography. J Chromatogr A 1360:76–81. https://doi.org/10.1016/j.chroma.2014.07.084

Ziaei E, Mehdinia A, Jabbari A (2014) A novel hierarchical nanobiocomposite of graphene oxide–magnetic chitosan grafted with mercapto as a solid phase extraction sorbent for the determination of mercury ions in environmental water samples. Anal Chim Acta 850:49–56. https://doi.org/10.1016/j.aca.2014.08.048