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Preconcentrations of Ni(II) and Co(II) by using immobilized thermophilic *Geobacillus stearothermophilus* SO-20 before ICP-OES determinations

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ABSTRACT

This study deals with the preconcentrations of Ni(II) and Co(II) ions in real samples using the solid phase extraction method (SPE) before their determinations by inductively coupled plasma optical emission spectrometry (ICP-OES). Thermophilic bacterium *Geobacillus stearothermophilus* SO-20 (Accession number: KJ095002), loaded with Amberlite XAD-4, was utilized as a novel biosorbent. Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscope (SEM) were employed for the investigation of the bacterial surface before and after Ni(II) and Co(II) biosorption. The experimental parameters were examined to find the best conditions. The retained Ni(II) and Co(II) ions on the biosorbent were eluted by using 5.0 ml of 1.0 mol l^{-1} HCl as the best eluent. The sorption capacities were found to be 16.8 mg g^{-1} for Ni(II) and 21.6 mg g^{-1} for Co(II). It was also successfully used for the quantification of Ni(II) and Co(II) in a river water sample, some vegetables and soil.

1. Introduction

Toxic metals are categorized as being environmental toxins because of their harmful effects on human health and the environment. They are cumulative poisons and are toxic even at low concentration (Ahmad et al., 2015; Hu, 2000). U.S. Agency for Toxic Substances and Disease Registry (ATSDR), lists lead (Pb), mercury (Hg), arsenic (As), and cadmium (Cd) as the most harmful metals according to their prevalence in the toxic waste sites and their toxicity severity (Fay & Mumtaz, 1996; Hu, 2005). The other toxic metals that are potentially dangerous for human health are nickel (Ni), cobalt (Co), copper (Cu), manganese (Mn), and chromium (Cr) (Martin, 2006; Nelson & Cox, 2000).

Ni, a hard, silvery-white colour metal, being an abundant natural element, can be combined with other metals, such as Cu, zinc (Zn), Cr, and iron (Fe), to form alloys. Excessive Ni affects some organ systems such as the respiratory, immunological, dermal and cardiovascular ones. Also known to be a potential human carcinogen (ATSDR; Demey, Vincent, & Guibal, 2017), Co is a naturally occurring element found in soil, water, rocks, animals and plants. It is used to produce alloys used in industry. Radioactive Co (^{58}Co and ^{60}Co), is employed widely in medical, commercial and nuclear industries (Someda, 2007). It is potentially carcinogenic for human beings.

The concentrations of toxic metals in environmental samples, such as water, plants and soil, must be lower than certain threshold concentrations due to their harmful effects (Okumuş et al., 2015). Therefore, accurate and precise determinations of toxic metal ions in natural patterns, such as water, food and soil, are the major challenge for analytical chemists because of their trace levels. Atomic spectroscopic techniques can be used for the determination of metal ions in different matrices but preconcentration procedures are often required due to insufficient sensitivities of the instruments. Co-precipitation, liquid-liquid extraction, electrochemical deposition, flotation, ion exchange, solid-phase extraction and chelating matrices have been utilized for the preconcentrations of metal ions (Kazi et al., 2009; Mousavi, Aibaghi-Esfahani, & Arjmandi, 2009).

The most common physicochemical methods, such as chemical reduction or oxidation, chemical precipitation, ion filtration, exchange, electrochemical treatment, freeze crystallization, membrane technology, reverse osmosis, electro dialysis and cloud point extraction, are employed for removing metals ions, including toxic ones. Most of these are not cheap or effective, particularly when the metal ions are not solved in a great volume of solutions (Mohammed, Kapri, & Goel, 2011).

The solid-phase extraction method (SPE) (based on the use of biomass as a biosorbent) has been applied for the preconcentration and recovery of metal ions. The SPE provides major advantages like high

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enrichment of metal ions, high recovery, removal of potentially interfering matrices, simple preparation of solid phases, low consumption of organic solvents, low cost, simplicity and environmental friendly approaches (Hosseini, Dalali, & Karimi, 2010; Kilinc, Dundar, Ozdemir, & Okumus, 2013; Salarian, Ghanbarpour, Behbahani, Bagheri, & Bagheri, 2014; Tuzen & Soylak, 2008). Various adsorbents, including Amberlite XAD resins (Tokalıoğlu, Papak, & Kartal, 2017), silica gel (Akhond, Absalan, Sheikhian, Eskandari, & Sharghi, 2006), activated carbon (Chand et al., 2009) and bentonite (Aytas, Yurtlu, & Donat, 2009), have been used for the SPE. Amberlite XAD adsorbents have been known as non-ionic polymeric support materials with superior chemical and physical characteristics such as having a high surface area, porosity, thermal stability, and also being economical and easily modified (Ahmad et al., 2015; Bhatti, Memon, Memon, Bhatti, & Solangi, 2017).

The biomass has been widely used for years for the preconcentration and separation of metals ions and several organic substances at very low levels because of remarkable adsorption characteristics such as having a high surface area and biosorption capacity (Fomina & Gadd, 2014).

In this study, *Geobacillus stearothermophilus* SO-20 loaded with Amberlite XAD-4, was used as a novel thermophilic biosorbent and, studied for the preconcentration and recovery of nickel and cobalt ions. The impacts of significant experimental factors were examined and the developed method was validated. Then, the recommended preconcentration method was utilized for a river water sample, several vegetables and soil.

2. Materials and methods

2.1. Instrumentation

ICP-OES was used for emission measurements at wavelengths of 231.604 nm and 228.616 nm for Ni(II) and Co(II), respectively (Perkin-Elmer, Optima 2100 DV, USA). Instrumental conditions were applied according to literature (Ozdemir, Kilinc, Poli, Nicolaus, & Guven, 2009). 1.0 cm × 10.0 cm polypropylene column was used for SPE experiments. A digital pH meter was used to measure the pH of the solutions (Mettler-Toledo, USA). A peristaltic pump was used to adjust the flow rate of solutions (Waters Marlow, USA). The surface morphology of the prepared materials was monitored using scanning electron microscopy (SEM) (LEO-Evo 40 XVP, Germany). The surface functionalities were investigated by Fourier transform infrared spectrophotometry (FT-IR) (Mattson Model 1000, UK).

The Dogfish muscle DORM-2 (National Research Council of Canada) and standard reference samples of fortified water (NWTM-15, High Purity Standard) were applied by the developed method to check the accuracy. Tap water and soil were sampled from Siirt, Turkey. Bonito, tomato, banana, cabbage, aubergine, redpepper, watermelon, parsley, chocolate, baby rice powder, coffee, gluten free biscuit, beef, meat and bovine liver samples were bought from local markets. 5.0 ml of concentrated HNO_3:HCl (1:1) was added to the sample for pre-digestion. They were heated until dryness. The samples were added to a 5.0 ml mixture of HNO_3:HCl:H_2O_2 (1:1:0.2) and then transferred to a temperature and pressure controlled microwave oven to complete the digestion. It was diluted to the required volume before SPE procedure.

2.2. SPE procedure

In this study, *G. stearothermophilus* SO-20, which was isolated from Gecek, Afyonkarahisar, Turkey, was used as a biosorbent. It was grown in nutrient broth with constant agitation at 55 °C during one day (rotary shaker, 120 rpm). The cultures were centrifuged and the pellets were washed two times with physiological saline (0.9%) and after that they were dried in an oven at 80 °C during one day. To transform dried cells into fine powder, they were milled in an agate mortar. They were then autoclaved at 121 °C for 15 min until complete death of the dried *G. stearothermophilus*. After that, the dried and autoclaved *G. stearothermophilus* were inoculated to the liquid media, and it was observed that there was no growth (complete death of the bacteria). Finally, Amberlite XAD-4 (750 mg) and dry biomass powder (200 mg) were mixed thoroughly in distilled water (7.5 ml). The column packing procedure was applied as mentioned in our previous study (Ozdemir, Kilinc, & Erdogan, 2010).

50.0 ml of solution containing 1.0 mg l^{-1} Ni(II) and Co(II) was applied to SPE column and was passed through it by utilizing a peristaltic pump. After that, distilled water (10.0 ml) was passed through the column. For determining the concentrations of Ni(II) and Co(II), 1.0 mol l^{-1} hydrochloric acid (HCl) was used as an eluent and then this solution was analyzed by ICP-OES.

3. Results and discussion

3.1. Surface studies

The surface morphologies of *G. stearothermophilus* SO-20 immobilized on XAD-4, Ni(II) on *G. stearothermophilus* SO-20 immobilized on XAD-4 and Co(II) on *G. stearothermophilus* SO-20 immobilized on XAD-4 were investigated by SEM. As can be seen from Fig. 1, a homogeneous surface has been obtained. Surface functionalities were investigated by FT-IR spectroscopy. The results were comparatively presented in Fig. 2. For XAD-4, the appearance of bands at 670–900 cm^{-1} are considered to be caused by aromatic C—H out-of-plane bending vibrations. The absorption frequencies of the C═C aromatic ring stretching vibrations are seen at 1512 and 1445 cm^{-1}. The peaks at approximately 1650, 3280 and 2925 cm^{-1} could be attributed to the carboxyl group, hydroxyl group and H-bonded —OH stretch of *G. stearothermophilus* SO-20. In Fig. 2 there was no significant difference (except as shifting of peaks) after the loading of Ni(II) and Co(II). Thus, it can be said that the sensitivity of the FT-IR is insufficient because the concentrations of metal ions were at low levels. Moreover, Ni(II) and Co (II) as borderline acids, could interact with borderline basic groups such as substitute alcohol and moderate basic groups on *G. stearothermophilus* SO-20.

3.2. Effect of pH

As a significant experimental parameter for the SPE process, the effect of pH values of the solution on the extraction efficiency of Ni(II) and Co(II) was investigated. For this purpose, a set of experiments were carried out using 50.0 ml of 1 mg l^{-1} Ni(II) and Co(II), with the pH range of 2.0–8.0. The recovery value was low, below pH 3.0, due to the protonation of the cell wall of the biomass which prevents the binding of analyte ions. The optimum pH was found to be 6.0 for Ni(II) and 5.0 and 6.0 for Co(II) ions (Fig. S1). In literature, it reports that the optimum pH for this kind of study is 3.0–6.0. Our results are compatible with the ones in literature. Under alkaline conditions, metal cations form hydroxide complexes (Ku & Chiou, 2002). It is thought that the biosorption efficiency of bacterial biomass decreases due to the increase of metal hydroxide precipitates. pH: 6.0 was selected for further studies because of achieving a high biosorption capacity.

3.3. Effect of sample flow rate

In SPE studies, the flow rate of the sample solution affects the interaction of analyte ions with the biosorbent. The duration of the analysis is directly affected by the flow rate. For this reason, it should be optimized. The influence of the flow rate of the sample solution was examined over the ranges of 1.0–6.0 ml min^{-1} at pH 6.0. The optimal flow rate was found to be 3 ml min^{-1} for the quantitative recoveries (Fig. S2). Higher flow rates decrease the recoveries due to less interactions of the analyte ions with the biosorbent. A flow rate of 3.0 ml min^{-1} was selected as the optimum one.

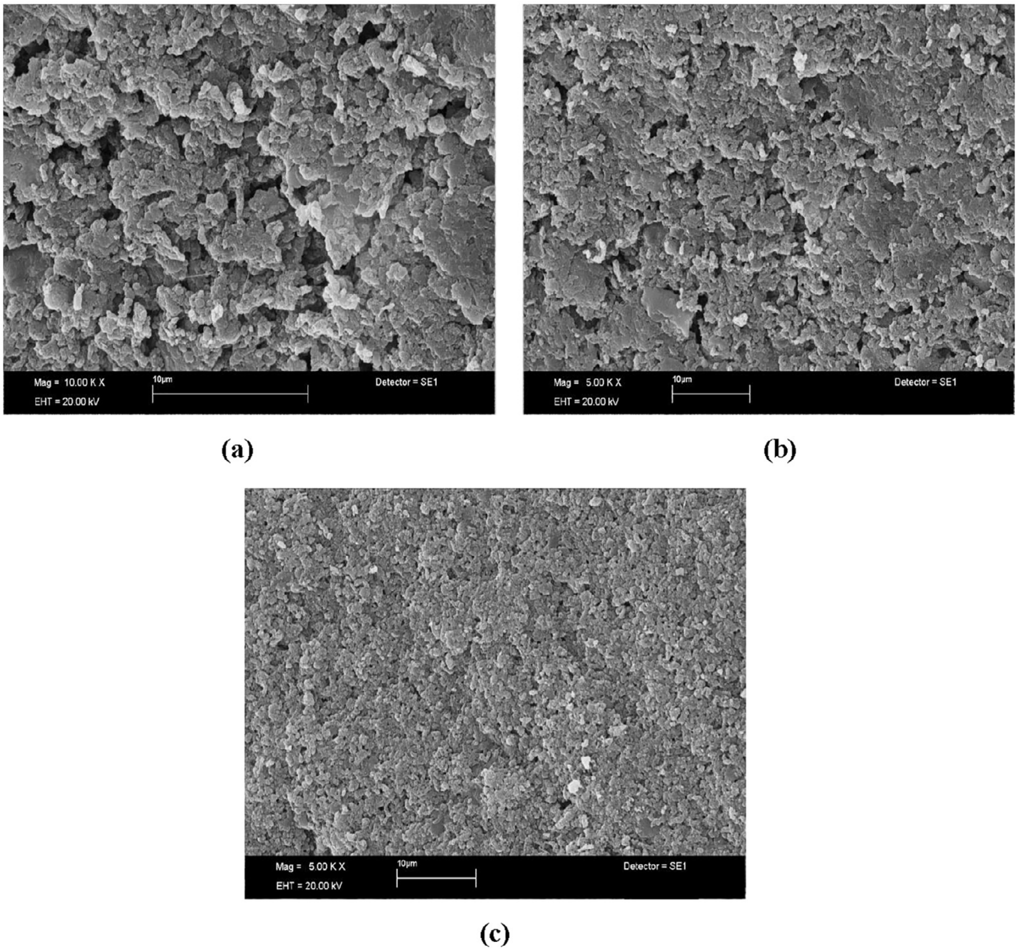

Fig. 1. Investigation of surface morphologies by SEM a) *G. stearothermophilus* SO-20 immobilized on XAD-4b) Ni(II) on *G. stearothermophilus* SO-20 immobilized on XAD-4, c) Co(II) on *G. stearothermophilus* SO-20 immobilized on XAD-4.

3.4. Influence of the amount of the biosorbent and resin

It is well known that the amount of the biosorbent is one of the most important experimental parameters in biosorption studies. For the optimization of the amount of *G. stearothermophilus* SO-20 as a biosorbent, it was experimented in the range of 50.0–400.0 mg. The uptake of Ni(II) and Co(II) ions increased due to the increase in the amount of the biosorbent. A maximum uptake was attained when the amount of the biosorbent was 300.0 mg (Fig. 3a). At higher amounts of the biosorbent, the metal uptake decreased because of the increase in the electrostatic interactions between the cells to agglomerate (Cho, Yoo, & Kim, 2004). Subsequent experiments were performed using 300.0 mg amount of *G. stearothermophilus* SO-20.

For the optimization of the adsorbent, under the best conditions, the effect of the resin (XAD-4) on the recoveries of Ni(II) and Co(II) ions was examined by changing the resin amounts from 50.0 to 300.0 mg (Fig. 3b). The results indicated that recoveries of Ni(II) and Co(II) ions increased up to 800.0 mg of resin, but higher amounts of resin did not affect the recovery of these ions. Therefore, the optimum quantity of resin was determined as 800.0 mg.

3.5. Biosorption capacity

The biosorption capacity of *G. stearothermophilus* SO-20 immobilized on XAD-4 for Ni (II) and Co (II) ions was determined under optimum conditions and its capacity was found to be 16.8 and 21.6 mg g^{-1}, respectively.

3.6. Effect of HCl and HNO_3 volume/concentration for elution

To acquire maximum recovery with minimum volume and concentration of the elution solution, the elution conditions must be optimized. For this purpose, HCl and HNO_3 were used as eluents. However, to prevent the degradation of biomass, the concentration of the eluent must be at the lowest possible level. The results are given in Fig. 4a and b. The recovery value of Ni(II) increased from 94.8% to 99.8%, when the concentration of 5.0 ml HCl increased from 0.5 mol l^{-1} to 1.0 mol l^{-1}. Likewise, the recovery value of Co(II) ions increased from 92.7% to 99.1%, when the concentration of 5.0 ml HCl increased from 0.5 mol l^{-1} to 1.0 mol l^{-1}. A 5.0 ml amount of 1.0 mol l^{-1} HCl was determined as the best eluent for further experiments.

3.7. Effect of sample volume

The real samples may contain trace level of metal ions. Therefore, the SPE technique is implemented to obtain a high preconcentration factor. Ideally, in this technique the sample volume should be higher. In order to determine the optimum sample volume on the extraction efficiency of metal ions, 25.0–500.0 ml of Ni(II) and Co(II) at the concentration of 1 mg l^{-1} solutions were passed through the column in the above mentioned optimum conditions. The recoveries of Ni(II) and Co(II) ions were found to be 97.8% and 98.7%, respectively, at a sample volume of 400.0 ml (Fig. S3). Thus, accepting 400.0 ml of the sample solution as the highest sample volume and using the column with 5.0 ml of 1.0 mol l^{-1} HCl as an eluent, a preconcentration factor of 80.0 can be reached.

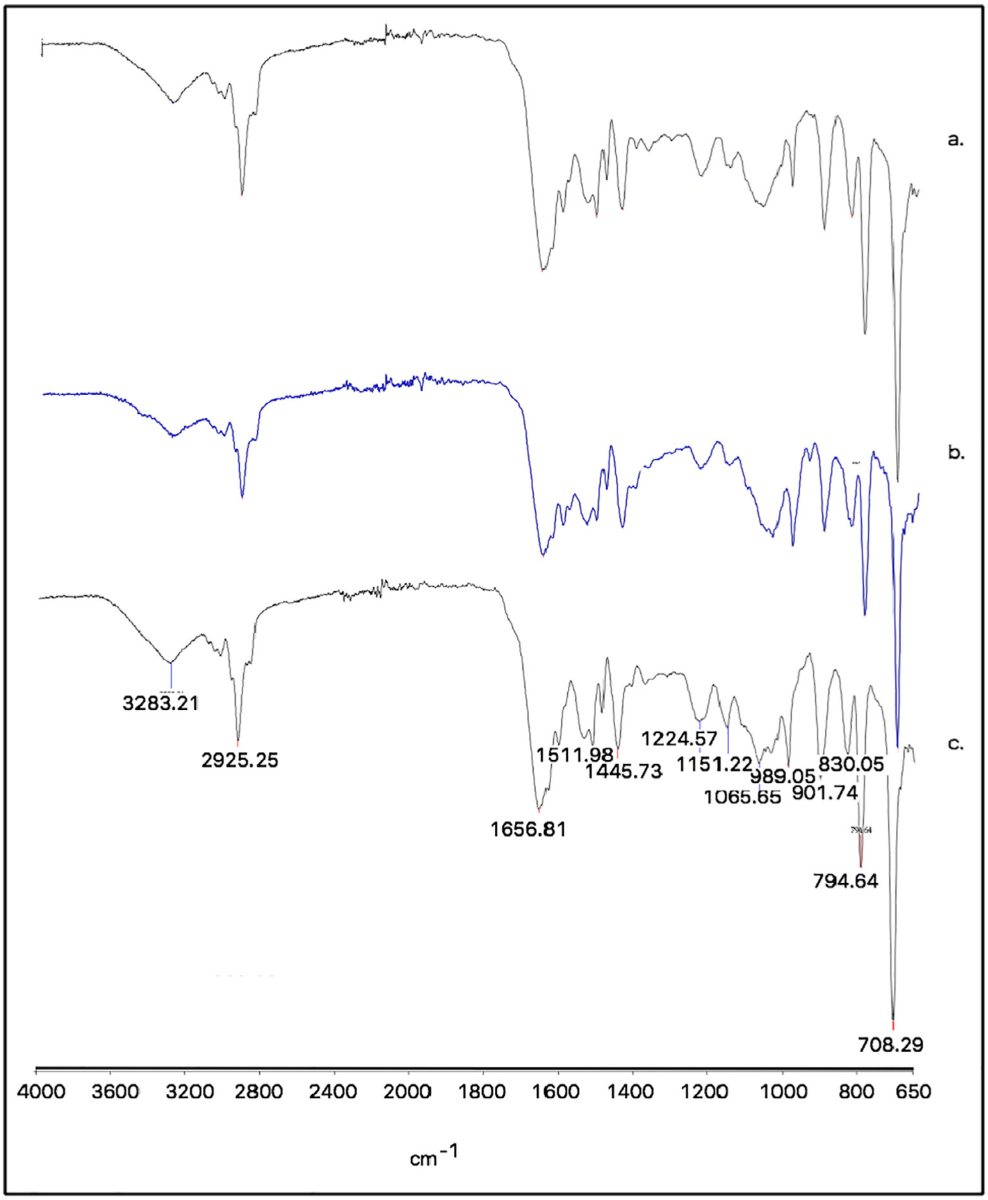

Fig. 2. Investigation of surface functionality by FT-IR a) *G. stearothermophilus* SO-20 immobilized on XAD-4b) Co(II) on *G. stearothermophilus* SO-20 immobilized on XAD-4, c) Ni(II) on *G. stearothermophilus* SO-20 immobilized on XAD-4.

3.8. Effect of coexisting ions

During the determination of the Ni(II) and Co(II) ions using ICP-OES by the proposed method, the interferences of some foreign ions were also investigated. The effect of some foreign ions, such as Na(I), K(I), Ca (II), Mg(II), Zn(II), Fe(II), Cd(II), Cu(II) and Al(III), on the recoveries of Ni(II) and Co(II) ions, was examined under the best experimental conditions. As can be seen in Table S1, tested foreign ions did not interfere with the determination of analytes.

3.9. Effect of column reuse

For the developed SPE method, the stability and reusability of the column is an important factor related to the economicterms. The SPE column, containing *G. stearothermophilus* SO-20 immobilized on XAD-4 was evaluated by monitoring the change in the recoveries of the analyte ions. As can be seen in Fig. S4, the recoveries of Ni(II) and Co(II) were 94.4% and 94.1%, respectively after the use of the column for 24 cycles.

3.10. Analytical performance and application

Under the best experimental conditions the analytical performance characteristics of the developed method were determined. Linear analytical curves were achieved in the concentration ranges of 0.25–12.5 ng ml^{-1} for Co(II) and Ni(II) with the correlation coefficients (r^2) as 0.9996 and 0.9997, respectively. The limit of detections (LOD) and the limits of quantitations (LOQ) were calculated as 0.022 and 0.072 ng ml^{-1} for Co(II) and 0.025 and 0.083 ng ml^{-1} for Ni(II), respectively. The preconcentration factors were 80 by considering the 400 ml of initial and 5.0 ml of final volume. A detailed comparison of the analytical characteristics of different methods developed by several authors (Duran, Senturk, Elci, Soylak, & Tufekci, 2009; Ghaedi, Karami, Shamsaldini, & Soylak, 2014; Karadas & Kara, 2013; Karimipour, Ghaedi, Sahraei, Daneshfar, & Biyareh, 2012; Losev, Buyko, Trofimchuk, & Zuy, 2015; Nomngongo, Ngila, Msagati, & Moodley, 2013; Su, Chen, He, & Hu, 2014) is presented in Table 1. By using *G. stearothermophilus* SO-20 immobilized on XAD-4, the use of synthetic

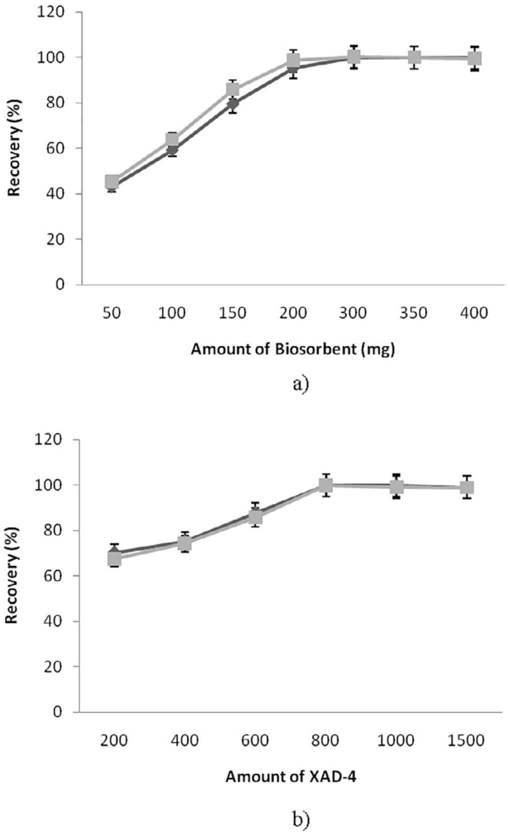

Fig. 3. a) Effect of the amount of the biosorbent on the recoveries of Ni(II) and Co(II) b) Effect of the amount of Amberlite XAD-4 on the recoveries of Ni(II) and Co(II).

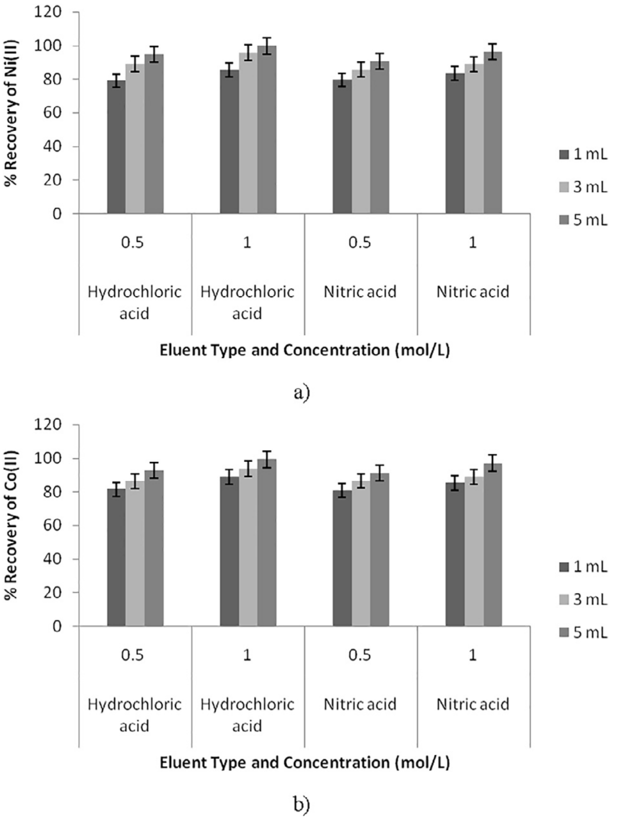

Fig. 4. Effect of the type, volume and concentration of elution solutions on recoveries of a) Ni(II) and b) Co(II) by using *G. stearothermophilus* SO-20 immobilized on XAD-4.

ligands, immobilized on different resin, could be eliminated. Thus, the recommended method had economic advantages and it could present a homogenous surface structure that supports reproducible results. Additionally, analytical characteristics of our method gave low LOD. So it can be concluded that the recommended method had comparable features and using it, it was possible to find a routine application for the monitoring of Co(II) and Ni(II) in different matrices.

NWTM-15 fortified water and DORM-2 dogfish muscle were applied to the developed method to check the accuracy. Co(II) and Ni(II) concentrations in NWTM-15 were determined to be 15.0 ± 1.1 and 17.8 ± 1.5 ng ml^{-1}, while they were certified as 15.1 and 18.1 ng ml^{-1}. Co(II) and Ni(II) concentrations in DORM-2 were determined as 0.18 ± 0.02 and 19.1 ± 2.3 µg g^{-1}, while they were certified as 0.182 ± 0.031 and 19.4 ± 3.1 µg g^{-1}. These results are in agreement with certified values and demonstrated that the proposed method has good accuracy. Tap water, bonito, tomato, banana, cabbage, aubergine, redpepper, watermelon, parsley, chocolate, baby rice powder, coffee, gluten free biscuit, beef, meat, bovine liver and soil samples were subjected to the developed SPE procedure. Sampling and digestion procedures are detailed in literature (Ozdemir, Kılınç, Okumuş, Çelik, & Soylak, 2017). Then concentrations of Co(II) and Ni (II) were determined by ICP-OES. Results are presented in Table 2. Co (II) and Ni(II) concentrations were found to be lower than the maximum allowed concentrations by WHO (Duz, Sagirdag, Celik, Hasan, & Kilinc, 2016) as 20 ng ml^{-1}. The maximum allowable Ni concentration was established as 75 mg kg^{-1} while it was not regulated for Co by EU (Maleki, Amini, Nazmara, Zandi, & Mahvi, 2014). However, there are no exact regulations on all of the foods. Additionally, exposure levels of the toxic metals strictly depend on their consumption amount as well as on their concentrations. Other important issues are the mobility and the oxidation states of the metal ions in environmental and food samples.

4. Conclusion

It has been concluded that *G. stearothermophilus* SO-20 immobilized on Amberlite XAD-4 as a biosorbent, demonstrated excellent efficiency for the preconcentrations of Ni(II) and Co(II) in food and environmental samples prior to determinations by ICP-OES. The best conditions were found as being a pH 6.0; a sample flow rate of 3.0 ml min^{-1}; 300.0 mg of *G. stearothermophilus* SO-20; 800.0 mg of resin (XAD-4) and 5.0 ml of 1 mol l^{-1} HCl as the desorption solution for immobilized bacterium. The detection limits were 0.025 ng ml^{-1} for Ni(II), and 0.022 ng ml^{-1} for Co(II), respectively under these conditions. The developed method was validated with two certificated reference materials and applied on some food and environmental samples. As a result, it can be stated that the novel process can be used as an alternative method for the preconcentrations of Ni (II) and Co (II) in real samples.

Declaration of interest

The authors report no declarations of interest. The authors alone are responsible for the content and writing of the paper.

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Table 1
Comparison of analytical characteristics of the preconcentrations methods for Ni(II) and Co(II).

Method	Instrument	LOD, ng ml^{-1}		PF[1]		Linear range, ng ml^{-1}		Refs.
		Ni(II)	Co(II)	Ni(II)	Co(II)	Ni(II)	Co(II))	
SPE on Amberlite XAD-4 resin anchored with 8-hydroxy-2- quinoline carboxaldehyde	FAAS	0.72	0.70	–	–	100–500	100–400	Karadas and Kara (2013)
SPE on ammonium pyrrolidynedithiocarbamate complexes accumulated on Amberlite XAD- 2000 resin	FAAS	0.23	0.21	200	200	50–6000	50–6000	Duran et al. (2009)
SPE on Amberlite XAD-7 resin impregnated with 2-(1-(4-chlorophenyl)-4,5-diphenyl-1H- imidazol-2yl)-4-nitrophenol	FAAS	2.5	2.5	150	150	15–240	20–240	Ghaedi et al. (2014)
SPE on gold nanoparticle loaded on activated carbon modified bybis(4-methoxysalicylaldehyde)-1,2-phenylenediamine	FAAS	2.4	2.4	200	200	20–360	20–310	Karimipour et al. (2012)
Solid phase microextraction on graphene oxide–silica composite coating hollow fiber	ICP-MS	0.02	0.00039	–	–	0.1–50	0.01–50	Su et al. (2014)
SPE on Dowex 50 W-x8 resin	ICP-OES	0.39	0.08	–	–	10–70	10–70	Nomngongo et al. (2013)
Silica based sorbent sequentially modified with polyhexamethylene guanidine and 2-(1,8-dihydroxy-3,6- disulfo-2-naphthylazo)benzenearsonic acid	ICP-OES	0.35	0.44	20	20	–	–	Losev et al. (2015)
SPE on Amberlite XAD-4 resin loaded with *Geobacillus stearothermophilus SO-20*	ICP-OES	0.025	0.022	80	80	0.25–12.5	0.25–12.5	This method

[1] Preconcentration factor.

Table 2
Application of developed method to real samples for the preconcentrations of Co(II) and Ni(II).

Samples	Co mg kg^{-1}	Ni mg kg^{-1}
Tap water	< LOD	< LOD
Tap water[1]	0.011 ± 0.001	0.010 ± 0.001
Bonito	0.20 ± 0.02	0.019 ± 0.004
Tomato	0.71 ± 0.04	0.33 ± 0.02
Banana	0.25 ± 0.03	0.14 ± 0.01
Cabbage	0.66 ± 0.01	0.22 ± 0.03
Aubergine	0.41 ± 0.01	0.27 ± 0.02
Red pepper	0.16 ± 0.02	0.16 ± 0.04
Watermelon	0.51 ± 0.04	0.16 ± 0.01
Parsley	0.60 ± 0.04	0.28 ± 0.02
Chocolate	0.044 ± 0.002	0.021 ± 0.003
Baby rice powder	0.069 ± 0.005	0.031 ± 0.06
Coffee	0.047 ± 0.004	0.029 ± 0.03
Gluten free biscuit	0.058 ± 0.005	0.019 ± 0.005
Beef	0.062 ± 0.04	0.025 ± 0.04
Meat	0.087 ± 0.006	0.028 ± 0.02
Bovine liver	0.076 ± 0.004	0.031 ± 0.06
Soil	13.7 ± 1.4	8.3 ± 0.07

[1] Spiked with known amounts of Co(II) and Ni(II) to give final concentrations as 0.010 mgl^{-1}.

Academic Writing Center of Mersin University, Turkey.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.foodchem.2018.05.103.

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