Food Chemistry 215 (2017) 447–453

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Simultaneous preconcentrations of Co^{2+}, Cr^{6+}, Hg^{2+} and Pb^{2+} ions by *Bacillus altitudinis* immobilized nanodiamond prior to their determinations in food samples by ICP-OES

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ARTICLE INFO

Article history:
Received 22 February 2016
Received in revised form 4 July 2016
Accepted 9 July 2016
Available online 9 July 2016

Keywords:
Bacillus altitudinis
Nanodiamond
Preconcentration
Co^{2+}
Cr^{6+}
Hg^{2+}
Pb^{2+}

ABSTRACT

A novel solid phase extraction method was developed for simultaneous preconcentration-separation of Co^{2+}, Cr^{6+}, Hg^{2+} and Pb^{2+} ions prior to their determinations in food samples by ICP-OES. Thermophilic *Bacillus altitudinis* immobilized nanodiamond was used as a new biosorbent. SEM and FT-IR analysis were studied to characterize the biosorbent. The optimum pH values of quantitative biosorption for Co^{2+}, Cr^{6+}, Hg^{2+} and Pb^{2+} were found to be 5.0, 6.0, 6.0 and 6.0, respectively. A flow rate of 3.0 mL min^{-1} was selected as optimum for all metal ions. 5 mL of 1 mol/L HCl was used as eluent. Preconcentration factor was achieved as 80. LODs were calculated as 0.071, 0.023, 0.016 and 0.034 ng mL^{-1}, respectively for Hg^{2+}, Co^{2+}, Cr^{6+} and Pb^{2+}. The biosorption capacities were calculated for Co^{2+}, Cr^{6+}, Hg^{2+} and Pb^{2+} as 26.4, 30.4, 19.5, and 35.2 mg/g, respectively. The developed method was successfully applied to food samples to determine analyte concentrations.

1. Introduction

The pollution of the environment by harmful heavy metal ions has attracted great attention over last few years. There are more than 20 heavy metals, but some of them, such as cadmium (Cd), lead (Pb) and mercury (Hg) are highly toxic and can cause damaging effects even at very low concentrations on living system (Kocaoba & Arısoy, 2011). Cobalt (Co) and chromium (Cr) are toxic when used in large amounts and long period exposure to both metals one of the reasons behind toxicity (Costa & Klein, 2006; Ozdemir et al., 2012). Direct determination of metal ions in food, soil and water samples by instrumental analysis is often difficult because of low concentration of trace metal ions and presence of interferences. Therefore, a separation and preconcentration technique is often required before determination (Mirabi, Dalirandeh, & Rad, 2015; Ozdemir et al., 2016).

Many sample pretreatment methods (e.g. solid-phase extraction, liquid-liquid extraction, precipitation, ion exchange and cloud-point extraction) are usable for separation and preconcentration of trace metals in different samples (Afkhami, Madrakian, & Siampour, 2006; Chen, Jin, & Wang, 1997; Okumus et al., 2015). Among these methods, solid-phase extraction (SPE) procedures are considered superior to other procedures for their simplicity, better efficiency and a higher preconcentration factor (Ozdemir, Okumus, Dundar, & Kilinc, 2013).

New solid materials have recently emerged as alternatives to traditional SPE sorbents with the aim of obtaining a more selective preconcentration of the target metal ions (Madrakian, Zadpour, Ahmadi, & Afkhami, 2015). The use of microbial biomass and metallic nanoparticles for the preconcentration and separation of heavy metals at trace levels are popular due to the good adsorption properties such as high surface area, high adsorption capacity and low temperature modification (Hassanpoor, Khayatian, & Azar, 2015; Kilinc, Dundar, Ozdemir, & Okumus, 2013a).

Nanodiamond has excellent mechanical properties, tunable surface structures and high surface areas. It is also non-toxic the surface area of nanodiamond is about 450 m^2 g^{-1}, which makes it

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http://dx.doi.org/10.1016/j.foodchem.2016.07.055
0308-8146/

potential superior adsorbents (Cicala, Massaro, Velardi, Senesi, & Valentini, 2014; Huang & Chang, 2004).

The present work aimed the use of thermophilic *Bacillus altitudinis* immobilized nanodiamond as a novel biosorbent for the separation and preconcentration of Co^{2+}, Cr^{6+}, Hg^{2+} and Pb^{2+}. Immobilized biosorbent was characterized by FT-IR and SEM. Various influencing parameters such as, pH value, amount of nanoparticles, amount of bacterial biomass, flow rate, volume of sample solution, and effect of major ions on the preconcentration of the tested metal ions were studied. The recommended method was validated through analysis of the certified and standard reference materials (DORM-2, DOLT-3, SRM 1643e, NCZ ZC73014, NCS DC73351). It was successfully utilized to the determination of cobalt, chromium, mercury and lead in water and food samples.

2. Materials and methods

2.1. Instrumentation

Concentrations of cobalt, chromium, mercury and lead were measured by ICP-OES at 228.616, 267.716, 194.168 and 220.353 nm, respectively (Perkin Elmer Optima™ 2100 DV, PerkinElmer, Inc., Shelton, CT, USA) under the instrumental operating conditions recommended by producer. pH of the solutions were measured by Mettler Toledo MPC 227 (Polaris Parkway, Columbus, OH, USA) digital pH meter. Filtration column (1.0 cm × 10.0 cm), equipped with polypropylene frites was used in SPE experiments. Peristaltic pump (Watson-Marlow 323 peristaltic pump, Cornwall, England) was used to adjust the flow rates of the sample and standard solutions to desired flow rates. SEM images were obtained on a LEO 440 SEM with an accelerating voltage of 20 kV to investigate surface morphology. The samples were covered with Au/Pd before SEM monitoring.

2.2. Reagents and solutions

1000 μg mL^{-1} stock solutions of Co^{2+}, Cr^{6+}, Hg^{2+} and Pb^{2+} were obtained from High Purity Standards, Charleston, SC, USA and diluted with doubly distilled water to lower concentrations. Unless stated otherwise, high purity reagents were used in experiments. All glass materials were kept permanently full of 1.0 mol L^{-1} of nitric acid when not in use. Concentrated HNO_3 (65%) H_2O_2 (35%), and HCl (36.5–38.0%) were supplied from (Sigma Aldrich, Germany).

Nanodiamond (No: 636428-1G) was purchased form Sigma Aldrich Co, St. Louis MO, USA. Dogfish muscle DORM-2, (National Research Council of Canada), dogfish liver DOLT-3 (National Research Council of Canada), simulated fresh water NIST 1643e (NIST), tea leaves NCSDC 73351 and tea leaves NCS ZC73014 China National Analysis Center for Iron and Steel) were applied the developed method to check the accuracy.

2.3. Growth of thermophilic Bacillus altitudinis sp. nov.

The thermophilic *Bacillus altitudinis* was isolated from hot spring mud sample of Billoris in Siirt, Turkey by Dr. Veysi Okumus and Dr. Sadin Ozdemir. Thermophilic *B. altitudinis* sp. nov. was grown in 500 mL bottles using Nutrient Broth (NB) for fermentation media. The fermentation media's pH was adjusted to optimum pH with 0.1 M HCl or NaOH. These glass bottles were autoclaved at 121 °C for 15 min. The glass bottles were inoculated with overnight culture of 5 mL cell suspension prepared in NB and then incubated at 55 °C and 120 rpm in shaker for one day.

2.4. Preparation of the dried dead cells and immobilized biosorbent

The fermentation media were centrifuged at 7.000 rpm for 10 min after one day incubation. After 10 min centrifugation, pellets were then washed twice with distilled water and dried in an oven at 80 °C for one day and then autoclaved at 121 °C for 15 min to determine the all of death of the bacteria. The autoclaved dried bacteria were inoculated to NB media and the no presence of any growth showed positive results (whole death of the cells). A 300 mg of dried and autoclaved bacterial biomass and 3 mL distilled water added into a 250 mL glass bottle and shaked at 8 h. After 8 h, 300 mg of nanodiamond put into the bottle and thoroughly mixed. The solid phase extraction column packing procedure was examined according to our previous study (Ozdemir, Erdogan, & Kılınç, 2010).

2.5. General sorption studies

A 50 mL model solution contain 10.0 ng mL^{-1} of Co^{2+}, Cr^{6+}, Hg^{2+} and Pb^{2+} were prepared and pHs of the solutions were adjusted to desired value. It was passed through the *B. altitudinis* immobilized nanodiamond SPE column. Peristaltic pump was used to pass the solution to column at adjusted flow rate. Then, 10.0 mL distilled water was passed through the column. 5.0 mL of 1.0 mol L^{-1} HCl was passed to column to eluate the retained Co^{2+}, Cr^{6+}, Hg^{2+} and Pb^{2+} ions before their determinations by ICP-OES.

2.6. Sample preparation

Tap water was sampled from Mardin-Turkey after flushing 5.0 min. Tigris River water was sampled in a 5.0 L PTFE bottle and acidified with 3 drop of concentrated nitric acid. The developed method was directly applied to 100 mL of tap, mineral and river water samples after pH adjustments. Apple juice, strawberry juice, energy drink, meat, chicken, flour, honey, milk, olive, white cheese, corn, tomato, potato, black tea samples were bought from local market. 10 mL of apple juice, strawberry juice, energy drink, milk and 5.0 g of meat, chicken, flour, honey, olive, white cheese, corn, tomato, potato, black tea samples were digested by microwave oven (Berghof MWS3-Berghof, Tubingen, Germany). 5.0 mL of HNO_3:HCl (1:1, v/v) was added to samples, and the mixture heated on a hot plate. It was evaporated until dryness and 6.0 mL of HNO_3:HCl:H_2O_2 (1:1:0.2, v/v/v) was added before transferring to a microwave vessel. They were heated to 170 °C by microwave irradiation and waited for 5.0 min. Then temperature was reached to 200 °C in 15 min and waited for 1.0 min. It was decreased to 100 °C and waited 20 min. After digestion the final volume was made up to 50.0 mL volume and the pH adjusted to the desired value before the SPE procedure. The SPE procedure was directly applied to a 100 mL portion of NIST 1643e water samples after pH adjustment. A 1.0 g portion of certified reference DORM-2, DOLT-3, NCSDC 73351 and NCS ZC73014 were digested using the same method described for the food samples.

3. Results and discussion

Surface morphologies of nanodiamond and *B. altitudinis* immobilized nanodiamond were investigated by SEM. Results were presented in Fig. 1a and b. It could be possible to discuss that microstructure of nanodiamond protected after immobilization of *B. altitudinis*. The major advantage of *B. altitudinis* immobilization was to increase the surface functionalities through the affinity to metal ions. Surface functionalities of nanodiamond and *B. altitudinis* immobilized nanodiamond were investigated by FT-IR. The comparison of overlay spectra was presented in Fig. 1c and d. In