Food Chemistry 276 (2019) 174–179

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

Preconcentrations and determinations of copper, nickel and lead in baby food samples employing *Coprinus silvaticus* immobilized multi-walled carbon nanotube as solid phase sorbent

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ARTICLE INFO

Keywords:
Coprinus silvaticus
Multiwalled carbon nanotube
Enrichment
Cu
Ni
Pb
Baby foods
ICP OES

ABSTRACT

Preconcentrations of Cu(II), Ni(II) and Pb(II) ions by using *Coprinus silvaticus* immobilized multiwalled carbon nanotube (MWCNT) were investigated. Effects of important parameters on preconcentration procedure were examined. The best pH values of for Cu(II), Ni(II) and Pb(II) were found to be 6.0, 6.0 and 4.0, respectively. Flow rate of sample solution was 2.0 mL min^{-1}, while desorption was achieved at 1.0 mL min^{-1} flow rate. Preconcentration factors were achieved as 60 for Cu(II), Ni(II) and 70 for Pb(II) (by dividing initial sample volume to final volume). LODs were calculated as 0.014, 0.016 and 0.093 ng mL^{-1}, respectively for Cu(II), Ni(II) and Pb(II). Accuracy of the method was checked by applying to certified reference samples. Inductively coupled plasma optical emission spectrometer (ICP OES) was employed for measurements of Cu(II), Ni(II) and Pb(II) in digested baby food samples.

1. Introduction

Toxic metals have been extremely discharged into the environment because off industrialization and have caused a great anxiety in worldwide. Mercury, cadmium, copper, lead and nickel are frequently determined in industrial polluted water which is based on from electroplating, metallurgical processes, ceramic, textile, glass, battery manufacture, pigment, fertilizers, petroleum refining, plastic manufacturing and mining (Ngah & Hanafiah, 2008).

The toxic metal ions are constant and permanent environmental pollutants because they cannot be destroyed and degraded. These metal ions such as chromium, nickel, lead, mercury, copper, manganese, cadmium can be harmful to ecological environments and water polluted by toxic metals causes a critical health problem for human being (Demirbas, 2008). Among the trace ions zinc, iron, cobalt, magnesium, molybdenum, and boron are essential to life while for chromium (except chromium(III)), arsenic, copper, mercury, nickel, lead, cadmium, and tin, no common knowledge of their biological functions exists and they are usually accepted as toxic (Ozdemir, Kilinc, Poli, Nicolaus, & Guven, 2009).

The extreme intake of copper by human causes to vigorous nausea, headaches, increased heart rate, hypoglycemia, hair loss, damage of kidney, and liver. The World Health Organization (WHO) proposed a maximum admissible level of copper in drinking water of 1.5 mg L^{-1} (Aman, Kazi, Sabri, & Bano, 2008). It was regulated for lead in infant formulae and follow-on formulae as 0.02 mg kg^{-1} (EU No. 1881, 2006).

Extreme concentrations of Ni may be danger to human in natural water sources. The US Environmental Protection Agency (EPA) recommends nickel not to exceed 0.5 mg L^{-1} in drinking water (Salem & Awwad, 2014). According to US EPA, Ni concentration in water should not exceed 0.02 mg L^{-1} (US EPA 1986). In the EU, maximum levels for nickel in food has not been regulated while it was determined as 20 µg L^{-1} for drinking water (EFSA, 2015). Lead is ubiquitous in the nature and is harmful at high levels. It causes toxicity to the nervous system, and influences the brain cells function (Rao, Rao, Seshaiah, Choudary, & Wang, 2008).

Importantly, toxic metal ions could accumulate in foods. Humans could exposure to metal ions by daily diet (Khamoni, Hamshaw, & Gardiner, 2017). Inadequate nutrition during infancy is one the main problem for disease (Mir-Marques, Gonzaloez-Maso, Cervera, & Guardia, 2015). From this point of view, monitoring and routine measurements of them are required. Atomic spectroscopic techniques are employed for measurements of metals include toxic ones. Separation and/or preconcentration step are generally required before

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https://doi.org/10.1016/j.foodchem.2018.07.123
Received 30 April 2017; Received in revised form 1 May 2018; Accepted 18 July 2018

measurements because of the fact that metal concentrations in food samples are at trace levels (Daşbaşı, Saçmacı, Ülgen, & Kartal, 2016).

Biological organisms can uptake metal ions, compounds, dyes, and particulates from solution with a process named biosorption. Living and dead biosorbents can also be used for toxic metal removal (Ozdemir et al., 2009; Ozdemir, Gul-Guven, Kilinc, Dogru, & Erdogan, 2010). Different developed techniques are available to make biosorbents adequate for process applications. Among these, immobilization processes have been applied to be practical for biosorption (Ozdemir & Kilinc, 2012; Ozdemir, Okumus, Dundar, & Kilinc, 2013). Liquid-liquid extraction, cloud point extraction, dispersive liquid-liquid microextraction, solid phase extraction are employed for preconcentrations of metal ions. The main disadvantage of liquid-liquid extraction method is the use of toxic ligands and solvents. Cloud point extraction is required more time such as heating, cooling and centrifugation than others methods. Solid phase extraction (SPE) of toxic metals by using immobilized biosorbent has been gradually used in environmental biotechnology due to numerous advantages such as decreasing the consumption of analysis time and quantity of chemicals, requesting more reusability, low limit of quantification, selective and sensitive methods (Bahar, Es'haghi, Nezhadali, Banaei, & Bohlooli, 2017; Tuzen, Sahiner, & Baki, 2016). *Agrobacterium tumefaciens*, *Bacillus thuringiensis*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Geobacillus stearothermophilus* were immobilized to different support materials such as Amberlite, nanomaterials, activated carbon etc (Ozdemir et al., 2013).

2. Materials and methods

2.1. Instrumentation and chemicals

Stock solutions of Cu, Ni and Pb at the concentration of 1000 μg mL^{-1} (High Purity Standards, Charleston, SC, USA) were used to prepare individual working solutions. All glass materials were washed with 1.0 mol L^{-1} of nitric acid and then with doubly distilled water before use. HNO_3 (65%) and H_2O_2 (35%) were supplied from E. Merck (Darmstadt, Germany) and used in the digestion procedures. Amberlite XAD-4 (Sigma Chemical, USA, 20–40 mesh, 780 m^2 g^{-1}) was used as a support material for immobilization of *Coprinus silvaticus* and interacted with HCl (4.0 mol L^{-1}) to remove the unwanted contaminants. 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). Acetic acid, phosphoric acid and boric acid (0.04 mol L^{-1} each of weak acids) were used to prepare Britton–Robinson buffers by adding the required amount of sodium hydroxide.

Concentrations of Cu, Ni and Pb were measured by inductively coupled plasma optical emission spectrometer (Optima™ 2100 DV, PerkinElmer, Inc., Shelton, CT, USA) at 327.393 nm, 231.604 nm and 220.353 nm wavelengths, respectively. pH of the solutions were measured by a MPC 227 model digital pH meter (Mettler-Toledo Co., Columbus, OH, USA). SPE experiments were performed in a filtration columns (1.0 cm × 10.0 cm), equipped with polypropylene frits. Marlow 323 peristaltic pump (Watson-Marlow, Wilmington, MA, USA) was used for passing the solutions through the column. Dogfish liver DOLT-3 (National Research Council of Canada), simulated fresh water NIST 1643e (National Institute of Standards and Technology), tea leaves NCS ZC73014 China National Analysis Center for Iron and Steel) and standard reference samples of fortified water (NWTM-15, High Purity Standard) were applied the developed method to check the accuracy.

2.2. Preparation of solid phase extraction (SPE) column

In this research paper, *Coprinus silvaticus*, collected from Sülün, Afyonkarahisar in Turkey, was used as a biomass for the enrichment of Cu(II), Ni(II) and Pb(II). To eliminate the contaminants from the

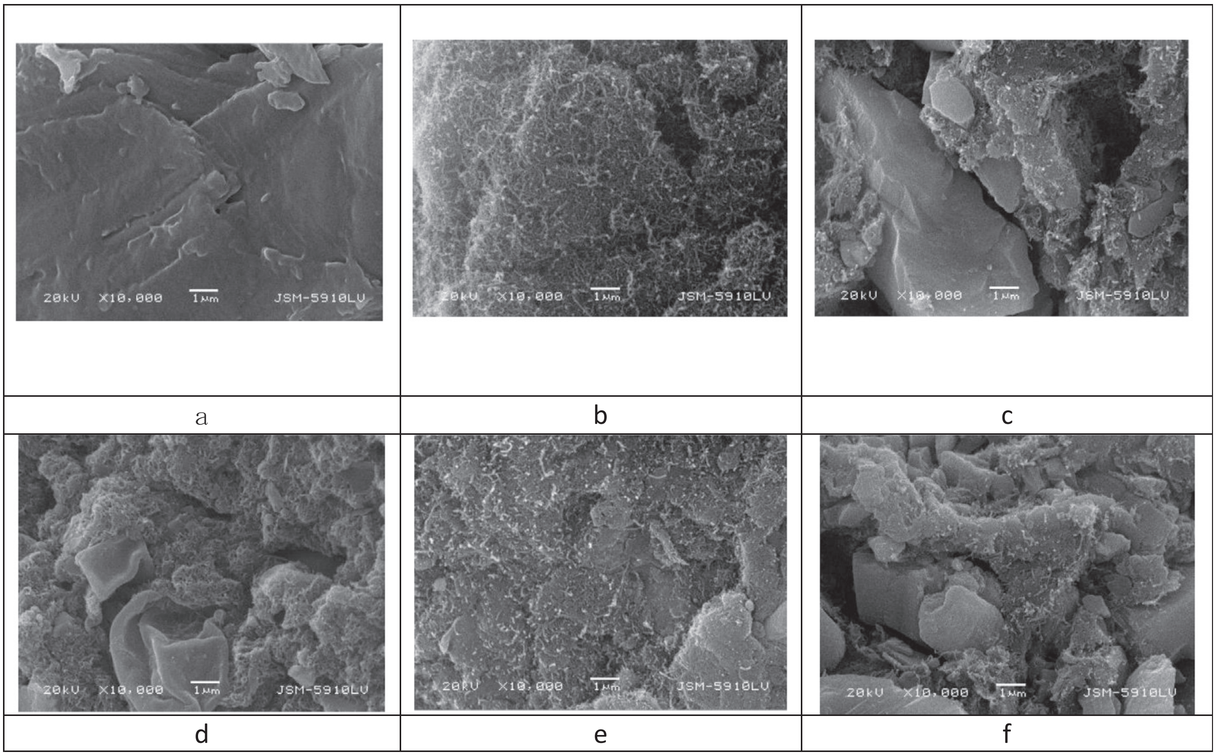

Fig. 1. Investigation of surface structure by SEM (a) *Coprinus silvaticus*, (b) multiwalled carbon nanotube, (c) *Coprinus silvaticus* immobilized multiwalled carbon nanotube, (d) *Coprinus silvaticus* immobilized multiwalled carbon nanotube with Cu(II), (e) *Coprinus silvaticus* immobilized multiwalled carbon nanotube with Ni(II), (f) *Coprinus silvaticus* immobilized multiwalled carbon nanotube with Pb(II).

biomass, it was cleaned two times with pure water. *C. silvaticus* was dried at 25 °C after cleaning. The dried *C. silvaticus* was milled in a porcelain mortar to get a fine powder. The powder *C. silvaticus* dried in a oven at 80 °C for 24 h to assess the whole death of the biomass. The oven dried biomass was then inoculated to malt agar at 25 °C for 2 days. The no growth of mycelia of *C. silvaticus* indicated positive results, meaning the whole death of the fungal biomass. The SPE column was prepared by a process from our prior investigations (Ozdemir et al., 2010). A 200-mg quantity of dry *C. silvaticus* was mixed with 200 mg multi-walled carbon nanotubes (MWCNT). After loading the fungal biomass to resin, it was sieved to get sizes of 20–60 mesh and packed in a solid phase extraction column. Before use, 10 mL of 1 mol L^{-1} HCl and 50 mL of pure water were passed through the column for conditioning and cleaning, respectively.

2.3. Procedure

A 50 mL model solution contain 10.0 ng mL^{-1} of Cu(II), Ni(II) and Pb(II) were prepared. After pH adjustments they were passed through *Coprinus silvaticus* immobilized multiwalled carbon nanotube SPE column by peristaltic pump. Then, 10.0 mL distilled water was passed through the column to control the efficiency of the extraction process. Biosorbed Cu(II), Ni(II) and Pb(II) ions were then eluated by 5.0 mL of 1.0 mol L^{-1} HCl. Concentrations of analytes in eluate were measured by ICP OES.

2.4. Sample preparation

A 300.0 mL portion of NWTM-15 and NIST 1643e were directly applied to SPE method after pH adjustment. A 0.25 g portions of NCS ZC 733014 tea leaves and DOLT3 (final volume was 50 mL) were applied the developed method after microwave digestion. Details on microwave digestion were reported in our recent study (Ozdemir, Kilinc, Celik, Okumus, & Soylak, 2016). Baby food samples were bought from supermarket and digested by microwave oven (Berghof MWS3-Berghof, Tubingen, Germany).

3. Results and discussion

3.1. Surface studies

Surface macro structures of *Coprinus silvaticus* and *Coprinus silvaticus* immobilized multiwalled carbon nanotube with and without Cu(II), Ni (II) and Pb(II) were monitored and results were presented in Fig. 1. However, there was no significantly differences in microstructures after immobilisation and biosorption of metal ions.

3.2. Effect of pH

Effective biosorption and solid phase extraction (SPE) of metal ions on a biomass surface is primarily dependent upon the pH range of sample solution. It is well-know that, the solutions pH affect the biomass surface area, charge of cell wall, extent of ionization, solubilization and speciation of metal ion in aqueous solutions (Al-bishri, Abdel-Fattah, & Mahmoud, 2012). So, the effect of pH on SPE of metal ions must be experimented. For this purpose, various pH ranges were studied from 2.0 to 8.0 for solid phase extractions of Cu(II), Ni(II) and Pb (II). The solid phase extraction of tested metal ions were decreased at lower pHs due to the increasing of the H^+ protons (S1). In addition to these, at higher pH, the retentions of Cu(II), Ni(II) and Pb(II) was decreased because of metal hydroxide precipitations (Ozdemir et al., 2009). The optimum pH was found to be 6.0, 6.0 and 4.0 for Cu(II), Ni (II) and Pb(II), respectively. Subsequently, in the further SPE studies, the solutions pH of 6.0, 6.0 and 4.0 were used for Cu(II), Ni(II) and Pb (II), respectively.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.foodchem.2018.07.123.

3.3. Flow rates of sample and desorption solutions

Flow rates of sample and desorption solution on the solid phase extraction processes are one of the most significant factors to get quantitative uptake and desorption, respectively (Tuzen, Karaman, Citak, & Soylak, 2009). The impact of the flow rates of sample and desorption solution on the biosorptions and recoveries of Cu(II), Ni(II) and Pb(II) from immobilized *C. silvaticus* on multi-walled carbon nanotubes were studied at various flow rate ranges (1–6 mL min^{-1}) too. As depicted from S2, when the flow rate was risedup from 2 to 4 mL min^{-1}, the biosorption percentages of Cu(II), Ni(II) and Pb(II) were reduced from 98.4% to 84.9%, 98.3% to 88.5% and 99.1% to 91.8%, respectively. It was observed that all tested metal ions were quantitatively desorbed at the desorption flow rate of 2 mL min^{-1}. In addition to these, effect of flow rates of desorption solution was also investigated and the most suitable desorption flow rate was found as 1 mL min^{-1} for all tested metal ions. The flow rates of 2 and 1 mL min^{-1}n were applied in the following uptakes and desorption studies, respectively for Cu(II), Ni(II) and Pb(II).

3.4. Effect of biosorbent and MWCNT dosage

The biosorbent amount is also a significant factor as it determines the biosorption capacity of biosorbent (Moyo, Guyo, Mawenyiyo, Zinyama, & Nyamunda, 2015). The influence of different amounts of biosorbent on the retentions of Cu(II), Ni(II) and Pb(II) is demonstrated in S3a. When the *C. silvaticus* amount increased from 50 to 150 mg L^{-1}, the biosorption percentages of Cu(II), Ni(II) and Pb(II) increased from 71.4% to 96.6%, 73.3% to 97.4% and 75.6% to 98.1% mg g^{-1} dry weight, respectively. Above 150 mg L^{-1}, decreasing was observed due to interference and competition of matrix ions (Al-Garni, 2005).

The impact of ranging amounts of MWCNT on the retention of Cu (II), Ni(II) and Pb(II) was also examined under the optimal conditions. It was observed that retention of Cu(II), Ni(II) and Pb(II) gradually increased up to 250 mg of MWCNT and reached a plateau thereafter (S3b). It was decided to use 250 mg of MWCNT for further studies.

3.5. Desorption studies

The desorption studies are major factor for the high concentration factor and have effect on reusability of immobilized biosorbent in solid phase extraction of metal ions (Ozdemir et al., 2016). The desorption of the biosorbed Cu(II), Ni(II) and Pb(II) ions on the immobilized *C. silvaticus* SPE column were examined under the optimum conditions. The results are represented in S4. Different concentration and volume of HCI and HNO_3 were used as desorption solution. With the concentration increasing from 0.5 to 1 mol L^{-1} HCI, the metal ion desorption percentages were increased from 95.1% to 100% for Cu(II), 95.8% to 100.2% for Ni(II) and 96.7% to 100% for Pb(II), respectively when the desorption solution volume was 5 mL. Quantitative recoveries (> 95%) were obtained for the all studied metal ions with 1 mol L^{-1} HCI. On the other hand, when using 5 mL 1 mol L^{-1} HNO_3 as desorption solution, the recovery percentages were lower than 5 mL 1 mol L^{-1} HCI. So, 5 mL 1 mol L^{-1} HCI was selected as desorption solution in further studies.

3.6. Effect of sample volume

The parameter of sample volume should be examined to get credible analytical results and high enrichment factor in solid phase extraction processes (Ziaei, Mehdinia, & Jabbari, 2014). For this purpose, various volumes of the sample were passed through the *C. silvaticus* loaded MWCNT solid phase extraction column. The biosorption percentages at various volumes are depicted in S5. The biosorption percentages did not show any change up to 200 mL. Quantitative recoveries (> 95%) were achieved with sample volume of 300 mL for Cu(II) and Ni(II) and 350 mL for Pb(II). Higher volumes was not adequate for the recoveries of all studied metal ions because of difficulty in the collection of biosorbent.

3.7. Stability of *C. silvaticus* loaded MWCNT solid phase extraction column

The reusability studies are represented in S6. The results shows that *C. silvaticus* loaded MWCNT used for the SPE column structure shows good stability in biosorption/desorption cycles using 1 mol L^{-1} HCl. These results are an evidence that the biosorption sites did not significant affect under the remarked acidity conditions. The reusability of the immobilized *C. silvaticus* can be similar as compared with our other immobilized fungal biosorbents studies, because the *C. silvaticus* loaded MWCNT solid phase extraction column was stable for 30 biosorption/desorption cycles.

3.8. Study on interferent ions

The impact of interference ions such as Na(I), K(I), Ca(II), Mg(II), Zn (II), Fe(II), Cd(II), Co(II) and Al(III) on the detection of Cu(II), Ni(II) and Pb(II) was studied. The concentration ratio for every interferent ions was as follows: 5000 for Na(I), K(I), 100 for Ca(II), Mg(II), 10 for Zn(II), Fe(II), and 5 for Cd(II), Co(II) and Al(III). The mixture solution of all tested ions and analytes were employed to SPE procedure. Recoveries of all of the tested metal ions biosorbed onto immobilized *C. silvaticus* on MWCNT in the presence of foreign species are given in S7. These interference ions had no important influences on the extraction and determination of Cu(II), Ni(II) and Pb(II) ions. Thus, it could be discussed that *C. silvaticus* loaded MWCNT has selectivity to Cu(II), Ni(II) and Pb (II). In our comments, it is based on the surface structure of bacterial surface and acidity of metal ions. Cu(II), Ni(II) and Pb(II) are accepted as borderline acid. According to hard and soft acid and bases theory, N-contain compounds should be rich on bacterial surface (Ozdemir et al., 2013).

3.9. Analytical features

The detection limits were calculated according to the regulation by of IUPAC (3Sb/b where Sb is the standard deviation of blank and b is the slope of calibration graph). Analytical features of SPE method based on *C. silvaticus* immobilized MWCNT as biosorbent for Cu(II), Ni(II) and Pb(II) were summarized in Table 1. LOQ for Cu(II), Ni(II) and Pb(II) in view of analyte mass per sample mass (by considering 0.25 g of sample) were as 0.92, 1.10, 6.20 ng g^{-1}. The relative standard deviations (% R.S.D) were found lower than 3.4%. Some analytical features of methods from literature were summarized in Table 2 for preconcentrations of Cu(II), Ni(II) and Pb(II). It is evident that the detection limits obtained with the *C. silvaticus* loaded MWCNT in SPE procedure were comparable to or even better than other chelating adsorbents. The eliminations of synthetic ligands, the use of toxic chemicals are the main advantage of our method. Thus, the developed method could be evaluated as environmentally-friend. 50 mL solution of Cu(II), Ni(II) and Pb(II) at the concentration of 100 mg L^{-1} was added with 200 mg of *C. silvaticus*. Loading capacities were calculated as 12.5 (196.9 µmol g^{-1}), 20.1 (342.5 µmol g^{-1}) and 16.5 (79.6 µmol g^{-1}) mg g^{-1}, respectively for Cu(II), Ni(II) and Pb(II) by considering the 0.25 g of sample weight and 50 mL of volume.

Table 1
Analytical features of the method.

Parameter	Cu(II)	Ni(II)	Pb(II)
Linear range, ng mL^{-1}	0.33–16.66	0.33–16.66	0.70–28.6
r^2	0.9929	0.9997	0.9996
LOD, ng mL^{-1}	0.014	0.016	0.093
LOQ, ng mL^{-1}	0.046	0.055	0.31
RSD, %	1.1	1.3	3.4
Loading capacity (mg g^{-1})	12.5	20.1	16.5
Preconcentration factor	60	60	70

The developed method was applied to the determination of Cu(II), Ni(II) and Pb(II) in certified/standard reference materials in order to verify the accuracy of the developed procedure. By considering the results presented in Table 3 that founded values were in good agreement with the certified concentration. Results were submitted to *t*-student test and it was clear to said that there was no systematic error on method (n = 3; t values were found lower than t_{critic} at 99% t-based confidence interval).

3.10. Application to food samples

The concentrations of metal ions are at trace levels in baby food samples. After digestion, direct measurements of some metal ions by AAS and/or ICP OES is problem due to insufficient sensitivity. By applying the SPE method, analytes in samples could be collected in small volume. Additionally, the matrix effect could be eliminated. Thus, ultratrace determination is possible through the sensitivity improvement. The developed procedure was applied for preconcentrations of Cu(II), Ni(II) and Pb(II) and following their measurements by ICP OES in baby food samples (Table 4). These samples were collected from supermarkets in Turkey. Some samples were spiked with known amounts of analytes. It could be concluded from the results that the recoveries for the addition of different concentrations of the elements of interest as high than 95%.

The highest value of Pb was detected in dry baby milk with fruit as 25.5 ± 4.0 ng g^{-1} that was just slightly higher than those regulated (20 ng g^{-1}) by European Communities Regulation No. 1881/2006 (Commission Regulation (EC) No. 1881) and Turkey (Resmi Gazete Sayı 28157). Pb level in baby milk powders consumed in Turkey were recently determined as lower from LOD (Daşbaşı et al., 2016). In our study, Pb was detected in baby food samples as in the range of 15.5–74.4 µg g^{-1} while it was lower than LOD for many of samples. Cu and Ni limits for baby foods are not regulated on these documents. Concentration of Cu in baby milk powders consumed in Turkey were recently determined as in the range of 0.19–0.27 µg g^{-1} (Daşbaşı et al., 2016). In this study, the highest Cu concentration was measured as 6.5 µg g^{-1} while the lowest was detected as 0.8 µg g^{-1}. Ni was only determined in two dry baby milk and an infant food with fruit as lower than 100 ng g^{-1}. Dietary intake of Ni was reported as 0.005 mg kg^{-1} of body weight per day (equal to 0.038 mg day^{-1}) for 0–12 month old infants and 0.134 mg day^{-1} (WHO, 2007).

Cu concentrations were determined in the ranges of 0.8–2.1 µg g^{-1}. The maximum allowances for Cu are 2 mg L^{-1} in drinking water by EU (European Union), while 1.1 mg day^{-1} Cu is determined for population reference intake by EU (PRI). Estimated Cu intakes were found 1.0–2.3 mg day^{-1} for males and 0.9–1.8 mg day^{-1} for females in European countries (European Food Safety Authority, 2006).

4. Conclusion

C. silvaticus immobilized MWCNT may be considered as an efficient biosorbent on SPE. The proposed method provides a simple, fast and cheap approaches. High preconcentration factors were achieved for Cu (II), Ni(II) and Pb(II) provide ultrace trace analysis of analytes in food samples. The developed method has high tolerance to metal ions that could be found in food matrices. Pb and Ni concentrations in some samples were found higher than allowable limits. Reusability of the column is another advantage. The developed method could be successfully applied to the preconcentration and determination of Cu(II), Ni(II) and Pb(II) in baby food samples as routine procedure. Therefore, studies surrounding this debate should continue as well.

Table 2
Comparative data from literature for the preconcentrations of Cu(II), Ni(II) and Pb(II).

Method	Ion	Linear range	LOD ng mL^{-1}	Instrument	Matrix	Ref.
Preconcentration on activated carbon, batch method	Cu	0.2–4	1.6	ICP-OES	Fruit	Feist and Mikula (2014b)
Suspension dispersive phase SPE	Cu	10–1000	1.5	FAAS	Water	Meng, Chen, and Yang (2015)
Coprecipitation	Cu	0.2–4	2.9	ICP-OES	Vegetables	Feist and Mikula (2014a)
Biomass based SPE	Cu	0.33–16.66	0.014	ICP-OES	Food, water	This method
Preconcentration on activated carbon, batch method	Ni	0.1–2	2.6	ICP-OES	Fruit	Feist and Mikula (2014b)
Suspension dispersive phase SPE	Ni	10–1000	1.7	FAAS	Water	Meng et al. (2015)
Microextraction by nanometer-sized ceria-coated silica–iron oxide	Ni	–	0.14[1]	ICP-OES	Water, urine	Dados, Paparizou, Eleftheriou, Papastephanou and Stalikas (2014)
Biomass based SPE	Ni	0.33–16.66	0.016	ICP-OES	Food, water	This method
Preconcentration on activated carbon, batch method	Pb	0.1–2	0.92	ICP-OES	Fruit	Feist and Mikula (2014b)
Coprecipitation	Pb	0.1–2	3.2	ICP-OES	Vegetables	Feist and Mikula (2014a)
Preconcentration via ion associated complexes	Pb	0.1–2	3.5	ICP-OES	Vegetables	Feist, Mikula, Pytlakowska, Puzio and Sitko (2012)
Biomass based SPE	Pb	0.7–28.6	0.093	ICP-OES	Food, water	This method

[1] LOQ.

Table 3
Application of the method to certified and standard reference materials.

Material	Cu(II)		Ni(II)		Pb(II)	
	Certified	Founded	Certified	Founded	Certified	Founded
NCSZC 73014, μg g^{-1}	18.6 ± 0.7	18.5 ± 0.9	3.4 ± 0.3	3.3 ± 0.25	1.5 ± 0.2	1.5 ± 0.2
NWTM-15, μg L^{-1}	18.3	18.1 ± 1.1	18.1	17.9 ± 1.2	11.8	11.7 ± 0.6
DOLT-3, μg g^{-1}	31.2 ± 1.0	30.4 ± 0.85	2.72 ± 0.35	2.6 ± 0.2	0.32 ± 0.05	0.31 ± 0.04
NIST 1643e, μg L^{-1}	22.76 ± 0.31	22.4 ± 0.8	62.41 ± 0.69	61.9 ± 0.48	19.63 ± 0.21	19.5 ± 0.9

Table 4
Cu(II), Ni(II) and Pb(II) amounts of different baby food samples (μg g^{-1}).

Sample	Cu(II) μg/g	Ni(II) ng/g	Pb(II) ng/g
Dry baby milk-1	1.2 ± 0.090	32.6 ± 2.8	<
Dry baby milk-1*	6.1 ± 0.50	81.4 ± 6.9	49.1 ± 3.4
Dry baby milk-2	0.9 ± 0.05	<	<
Dry baby milk-3	1.5 ± 0.11	45.4 ± 4.1	<
Dry baby milk (organic)	1.1 ± 0.080	<	<
Dry baby milk with fruit-1	1.5 ± 0.11	<	25.5 ± 4.0
Dry baby milk with fruit-1*	6.5 ± 0.44	48.7 ± 2.9	74.4 ± 5.4
Dry baby milk with fruit-2	1.5 ± 0.10	<	<
Dry baby milk with fruit-3	1.4 ± 0.12	<	<
Infant food with fruit-1	1.2 ± 0.10	<	<
Infant food with fruit-2	2.1 ± 0.15	<	<
Infant food with fruit-3	1.0 ± 0.06	70.1 ± 5.6	<
Infant food with fruit-3*	4.9 ± 3.2	115.1 ± 10.1	48.2 ± 2.9
Infant biscuit-1	2.1 ± 0.12	<	<
Infant biscuit-2	1.1 ± 0.040	<	<
Infant biscuit-3	0.8 ± 0.009	<	15.5 ± 1.2
Infant biscuit-3*	5.8 ± 0.41	50.1 ± 4.3	64.4 ± 5.0

* Spiked with 5 μg g^{-1} Cu and 50 ng g^{-1} Ni and Pb.

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