RESEARCH ARTICLE **Open Access**

CrossMark

Mucor pusillus immobilized Amberlite XAD-4 biocomposites for preconcentration of heavy metal ions by solid-phase extraction method

Sıtkı Baytak[1], Abdul Majid Channa[1,2*] and Ebru Çamuroğlu[3]

Abstract

Background: Solid phase extraction has been an effective tool for the determination of metal ions at trace or sub trace level from environmental aquatic streams. Sensitivity, accuracy, versatility and reusability of adsorbent entitle the solid phase as effective technique for the determination of metal ions.

Methods: A solid phase extraction procedure has been described for the determination of Cd, Cu, and Pb by High Resolution–Continuum Source Flame Atomic Absorption Spectrometry HR-CS FAAS using a mini-column of *Mucor pusillus* (Lindt., 1886) immobilized on Amberlite XAD-4. Method has been optimized by changing the pH of analyte solution, solid phase dosage, volume of eluents, flow rate of sample solution and volume of the sample solutions.

Results: The recoveries of Cd, Cu, and Pb under the optimum conditions were 99±3%, 97±2% and 96±2%, respectively. The resulting preconcentration procedure ensured a 50-fold improvement in the sensitivity of the elements. The detections limits were 62, 74 and 235 ng/mL for Cd, Cu, and Pb before enrichment, respectively. The method was validated by analysis of tomato leaves reference materials (SRM 1573a).

Conclusions: The proposed enrichment method has been successfully applied for the determination of Cd, Cu, and Pb in tomato leaves and water samples with a relative error ≤8%. This method is simple, sensitive, and accurate especially for water sample, only 200 mg of sorbent are required to capture the analytes. It can be concluded that the use of *Mucor pusillus* (Lindt., 1886) enhanced the sorption ability of Amberlite XAD-4 resin for the retention of Cd, Cu, and Pb.

Keywords: *Mucor pusillus*, Amberlite XAD-4, Heavy metal, Preconcentration, Solid-phase extraction

Background

Determination of metal ions in the environmental samples at trace or sub trace levels has been a challenging task for researchers. Analytical determination needs specificity, sensitivity, accuracy, and versatility. Many instrumental methods have been used to find the direct determination of metal ions, but it seems impossible because of matrix interferences and low concentration of metal ions in the environmental samples. These problems can be solved by applying effective separation and preconcentration techniques for the quantification of metal ions up to the detection limits. Various methods have been discussed and applied for the preconcentration of metal ions, including liquid-liquid extraction (LLE) (Anthemidis and Ioannou 2009), coprecipitation (Saracoglu et al. 2012), cloud point extraction (CPE) (Hongbo et al. 2013), and solid-phase extraction (SPE) (Sahmetlioglu et al. 2014; Baytak and Arslan 2015; Baytak and Kasumov 2017),which are used to solve these problems of trace metal determinations. SPE has been a most promising technique because of its simplicity, use of small volume of solvent, and ability to obtain a

* Correspondence: channa_abdulmajid@yahoo.com
[1]Department of Chemical Engineering, Faculty of Engineering, Suleyman Demirel University, 32260 Isparta, Turkey
[2]Institute of Advanced Research Studies in Chemical Sciences, University of Sindh, Jamshoro, Pakistan
Full list of author information is available at the end of the article

Baytak *et al. Journal of Analytical Science and Technology* (2018) 9:9

Page 2 of 6

high preconcentration factor and high speed (Baytak and Arslan 2015; Baytak and Kasumov 2017; Krawczyk et al. 2014) .Various adsorbents have been investigated in SPE such as multi-walled carbon nanotubes (Li et al. 2013; Alothman et al. 2012; Wang et al. 2011), magnetic nanoparticles (Asgharinezhad et al. 2014; Khajeh 2009), solid sulfur (Parham et al. 2009), cotton (Faraji et al. 2009), modified porous materials (Matbouie et al. 2013; Taghizadeh et al. 2013; Pereira et al. 2010), and Amberlite XAD resins for preconcentration and separation of trace metal ions from various media (Baytak and Turker 2005a).

Chelating polymeric resin can be modified by immobilizing suitable and selective ligands onto functionalized polymeric solid surfaces. Many chelates have been suggested using Amberlite XAD polymer as a solid support because of higher adsorption capacity. Functionalized polymers having sound stability and higher affinity for the uptake of metal ions have attracted the attention of researchers. Various ligands have been used to develop Amberlite XAD as a solid support for the metal ions such as hydroxamic acid (Kumar et al. 2011), 2-amino-5-hydroxy benzoicacid (Sabarudin et al. 2007), 2, 6-diacetylpyridine (Karadas et al. 2011), and fluorinated β-diketone (Waqar et al. 2009).

Biosorption is a technique that is used to make complexes using biological materials with metal ions, using their functional groups (Krishnani et al. 2008; Pires et al. 2011). Recently, it has been investigated using various microbial biomasses for the preconcentration of trace metals (Calero de Hoces et al. 2013; Baytak et al. 2011; Tuzen et al. 2008; Baytak and Turker 2005b; Baytak et al. 2014; Baytak and Turker 2009; Rajfur et al. 2010; Vilar et al. 2008) Microorganisms such as yeast (Baytak et al. 2011; Tuzen et al. 2008; Baytak and Turker 2005b), fungus (Baytak et al. 2014; Baytak and Turker 2009), and algae (Rajfur et al. 2010; Vilar et al. 2008) have been applied for the effective concentration of metal ions from the water system (Bakırcıoğlu et al. 2010; Wang and Chen 2009).

In the present study, a new method has been developed for the preconcentration of Cd, Cu, and Pb using *Mucor pusillus* (Lindt., 1886) immobilized Amberlite XAD-4 as a solid phase by HR-CS FAAS.

Methods
Apparatus and reagents
An Analytical Jena model HR-CS FAAS was used for the determination of the analytes. Doubly distilled water and analytical reagent grade chemicals were used. Cd, Cu, and Pb stock solutions (100 μg/mL) were prepared by dissolving the appropriate amounts of 1000 μg/mL Cd, Cu, and Pb (Specx Certiprep) in 2% HNO_3. The working solutions were prepared by dilution from the stock solution. Amberlite XAD-4 (Sigma Chem. 20–40 mesh, 780 m^2/g) was used as a substrate for the immobilization of *Mucor pusillus* (Lindt., 1886).

Preparation of solid phase
Mucor pusillus (Lindt., 1886) was grown, prepared, and immobilized according to the procedure given by Baytak and Turker (2009). Two hundred milligrams of Amberlite XAD-4 loaded with *Mucor pusillus* (Lindt., 1886) was packed in a glass column (8 mm i.d and 200 mm length). Before using, 1 mol/L HCl solution and doubly distilled deionized water were passed through the column in order to clean it. Then, the column was conditioned for the optimization of pH experiments.

Preconcentration procedure
An aliquot of a solution (100 mL) containing 20 μg of Cd, 20 μg of Cu, and 20 μg of Pb was taken, and the pH was adjusted to the desired value with hydrochloric acid or ammonia. The resulting solution was passed through the column by a flow rate adjusted to the desired value. The retained metal ions were then eluted from the solid phase with 10 mL of 1 mol/L HCl solution. This solution was aspirated into an air-acetylene flame for Cd(II), Cu(II), and Pb(II) determinations by HR-CS FAAS. The Amberlite XAD-4 loaded with *Mucor pusillus* (Lindt., 1886) was used repeatedly after washing with 1 mol/L HCl solution and distilled water, respectively.
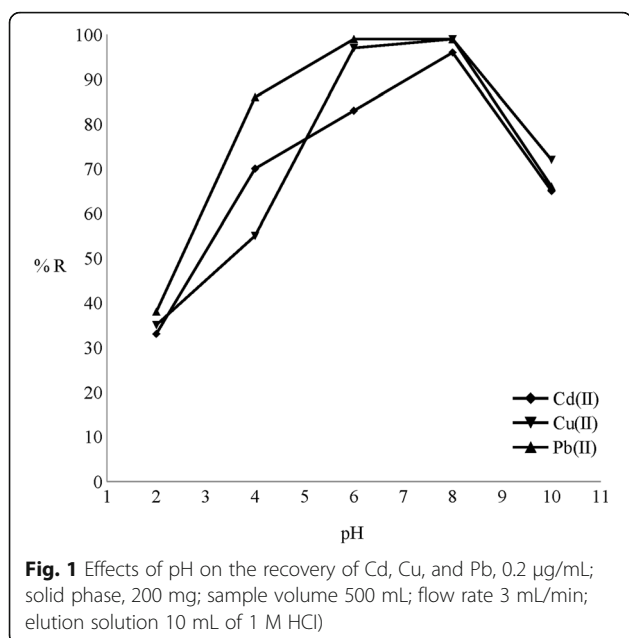
Results and discussion
Effect of pH
The retention of Cd, Cu, and Pb metal ions on the solid phase was studied as a function of pH, amount of solid phase, amount and type of elution solution, flow rate of sample solution, and volume of sample solution. The pH of Cd, Cu, and Pb ion solutions were optimized from 6 to 8, while solid-phase dosage 200 mg, eluent 10 mL (1 M HCl), flow rate of sample solution 2 mL/min, and sample volume 500 mL were kept constant. Maximum recovery was obtained at about pH 8 for all metal ions as shown in Fig. 1.

Effect of solid-phase dosage
The effect of solid-phase dosage was investigated in the range 50–400 mg. It was found that the recoveries gradually increased up to 200 mg of solid phase and reached plateau above 200 mg. Therefore, 200 mg of solid phase was found to be optimum for the preconcentration of all metal ions.

Baytak et al. Journal of Analytical Science and Technology (2018) 9:9

Page 3 of 6

Fig. 1 Effects of pH on the recovery of Cd, Cu, and Pb, 0.2 μg/mL; solid phase, 200 mg; sample volume 500 mL; flow rate 3 mL/min; elution solution 10 mL of 1 M HCl)

Effect of type and volume of elution solutions

In order to optimize the elution study, different eluents were used like HCl and HNO_3. Concentration and volume of these eluents were varied to investigate the effect of eluent type, volume, and concentration. As a result of these experiments, 10 mL of 1 M HCl solution was found to be satisfactory for these metals as shown in Table 1.

Table 1 Effect of the type, concentration, and volume of the elution solution on the recovery of Cd, Cu, and Pb ions [sample volume, 50 mL; amount of the metals 10 μg of Cd, Cu, and Pb; pH 8 for Cd, Cu, and Pb]

Element	Type of eluent	Volume (mL)	Concentration (mmol mL^{-1})	R%[a]
Cd	HCl	5	1	86
		10	1	99
	HNO_3	5	1	82
		10	1	94
Cu	HCl	5	1	84
		10	1	97
	HNO_3	5	1	80
		10	1	90
Pb	HCl	5	1	86
		10	1	96
	HNO_3	5	1	78
		10	1	90

[a]Mean of three determinations

Effect of flow rates of sample solutions

The retention of metal ions on a solid phase depends upon the flow rate of sample solution. Flow rate was examined under optimum conditions (pH, eluent type, dosage, and eluent volume). The solution was passed through the column with a flow rate adjusted in a range of 0.5–6 mL min^{-1}. The optimum flow rate was found to be 3 mL min^{-1} for all of the analytes. The flow rate of elution solution used was 3 mL min^{-1}.

Effect of the volume of sample solutions

In order to determine the maximum applicable volume of sample solution, the effect of change in the volume of sample solution passed through the column on the retention of analytes was investigated; 50, 100, 250, 500, 750, and 1000 mL of sample solutions containing 20 μg of Cd, Cu, and Pb were passed through the column. It was found that all of the metal ions up to 500 mL of sample solution could be recovered quantitatively. At higher sample volumes, the recoveries decreased gradually with increasing volume of sample solution. Because the elution volume was taken 10 mL, a preconcentration factor of 50 was obtained for all of the analytes. However, preconcentration factor with *Agrobacterium tumefaciens* immobilized on Amberlite XAD-4 has been reported 25. So, this method presents improved enrichment procedure with higher preconcentration factor (Baytak and Turker 2005a).

Analytical performance of the method

Under the optimum conditions, the precision of the method has been investigated. The recovery of the analytes were found as 99 ± 3%, 97 ± 2%, and 96 ± 2% for Cd, Cu, and Pb, respectively, with relative standard deviation lower than 2%. The accuracy of the proposed method was checked by analyzing the certified reference material (SRM-1573a tomato leaves) (Table 2). The method was applied for the determination of Cd, Cu, and Pb in water and tomato leaves' samples. Results were shown in Tables 3 and 4. Method validation was confirmed by the good agreement between the results of the proposed method and certified values of Cd, Cu, and Pb.

Table 2 Determination of Cd, Cu, and Pb in (SRM-1573a tomato leaves) reference material

Element	Certified (mg/kg)[a]	Found (mg/kg)	Relative error, %
Cd	1.52 ± 0.04	1.45 ± 0.02	− 5
Cu	4.70 ± 0.14	4.52 ± 0.15	− 4
Pb	4.0 ± 0.1	3.72 ± 0.08	− 7

Pb was added to the solutions of SRM-1573a tomato leaves
[a]Mean of five determinations at 95% confidence level $(\overline{x} \pm ts/\sqrt{N})$

Baytak *et al. Journal of Analytical Science and Technology* (2018) 9:9

Page 4 of 6

Table 3 Determination of Cd, Cu, and Pb in tomato leaves (0.5 g)

Element	Added (μg/g)[a]	Found (μg/g)[b]	Relative error, %
Cd	–	N.D	–
	10	9.4 ± 0.15	− 6
Cu	–	4.8 ± 0.1	–
	10	13.7 ± 0.3	− 7
Pb	–	N.D	–
	10	9.3 ± 0.2	− 7

N.D not detected

[a]Mean of five determinations at 95% confidence level ($\bar{x} \pm ts/\sqrt{N}$)

[b]Shows the concentration of metal ions in tomato leaves and Kızılırmak river water samples

The effect of column reuse

The stability and potential recyclability of the column were assessed by monitoring the change in the recoveries of Cd, Cu, and Pb through several adsorption-elution cycles. Each cycle was performed by passing 50 mL of each analyte solution through the column and then stripping the analytes by appropriate eluent. The procedure was carried out ten times in a day, and the next ten runs were made 1 day later, and so on. The columns were stored in doubly distilled deionized water. The column seems to be relatively stable up to 40 for Cd and Cu and 35 runs for Pb. This biomass seemed better than the other biomass reported earlier (Baytak and Turker 2005a).

Effect of interfering elements

Interference study was carried out to examine the effect of interfering ions; alkaline and alkaline earth elements were

Table 4 Determination of Cd, Cu, and Pb in tap water and Kızılırmak river water samples (volume of samples 250 mL)

Samples	Element	Added (μg/L)[a]	Found (μg/L)[b]	Relative error, %
Tap water	Cd	–	N.D	–
		10	9.5 ± 0.2	− 5
	Cu	–	12.3 ± 0.4	–
		10	20.6 ± 0.5	− 8
	Pb	–	N.D	–
		10	9.4 ± 0.3	− 6
River water	Cd	–	N.D	–
		10	9.3 ± 0.3	− 7
	Cu	–	20.4 ± 0.6	–
		10	28.7 ± 0.7	− 6
	Pb	–	N.D	–
		10	9.2 ± 0.2	− 8

N.D not detected

[a]Mean of five determinations at 95% confidence level ($\bar{x} \pm ts/\sqrt{N}$)

[b]Shows the concentration of metal ions in tomato leaves and Kızılırmak river water samples

added to the synthetic samples containing Cd, Cu, and Pb. Nitrate or chloride salts of interfering elements were added to the sample solutions. The concentration of analytes was kept constant, and the concentration of interfering ions was used in the range of 2–1000 μg mL^{-1}. It can be seen in the Table 5 that there is no significant effect of interfering ions on the recovery of analytes.

Table 5 Effect of some ions on the recovery of Cd, Cu, and Pb [sample volume, 50 mL; amount of the metal ion, 10 μg; pH 8]

Interfering ion concentration (μg mL^{-1})	Interfering ion concentration (μg mL^{-1})	Recovery (R%)[a]		
		Cd	Cu	Pb
–	–	99	97	96
Na$^+$	25	98	96	96
	50	98	96	95
	500	96	95	95
	1000	95	94	93
K$^+$	25	98	97	96
	50	98	97	96
	500	96	96	95
	1000	93	95	95
Mg^{2+}	2	98	97	96
	5	97	97	94
	10	94	93	92
Ca^{2+}	2	98	97	96
	5	96	96	94
	10	94	92	93
Co	5	98	97	96
	10	97	97	96
	25	96	95	94
Cr	5	98	97	96
	10	97	96	95
	25	96	96	94
Fe	5	98	97	96
	10	97	97	95
	25	96	95	92
Mn	5	98	97	96
	10	97	97	95
	25	97	96	92
Ni	5	98	97	96
	10	97	96	95
	25	95	97	93
Zn	5	98	97	96
	10	97	96	94
	25	96	95	92

[a]Mean of three determinations

Baytak *et al. Journal of Analytical Science and Technology* (2018) 9:9

Page 5 of 6

Conclusions

The proposed enrichment method has been successfully applied for the determination of Cd, Cu, and Pb in tomato leaves and water samples with a relative error of ≤ 8%. This method is simple, sensitive, and accurate especially for water sample; only 200 mg of sorbent are required to capture the analytes. It can be concluded that the use of *Mucor pusillus* (Lindt., 1886) enhanced the sorption ability of Amberlite XAD-4 resin for the retention of Cd, Cu, and Pb. By using bioadsorbent, higher preconcentration factors have been obtained. Present study provides convenient and time-saving preconcentration technique; only 30 min is required for recovery and regeneration of biosorbent.

Availability of data and materials

The data and the contents of our manuscript will be available for the readers of the *Journal of Analytical science and Technology*.

Authors' contributions

Authors have done a team work to carry out this study. Experimental studies has been carried out by AMC and EÇ. The study has been supervised by SB and the the manuscript has been written jointly by AMC and SB. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Author details

[1]Department of Chemical Engineering, Faculty of Engineering, Suleyman Demirel University, 32260 Isparta, Turkey. [2]Institute of Advanced Research Studies in Chemical Sciences, University of Sindh, Jamshoro, Pakistan. [3]Department of Chemistry, Faculty of Science and Arts, Nevsehir Haci Bektaş Veli University, 50300 Nevsehir, Turkey.

References

Alothman AA, Habila M, Yilmaz E, Soylak M. Solid phase extraction of Cd(II), Pb(II), Zn(II) and Ni(II) from food samples using multiwalled carbon nanotubes impregnated with 4-(2-thiazolylazo) resorcinol. Microchim Acta. 2012;177:397–403.

Anthemidis AN, Ioannou KIG. Recent developments in homogeneous and dispersive liquid–liquid extraction for inorganic elements determination. A review Talanta. 2009;80:413.

Asgharinezhad AA, Mollazadeh N, Ebrahimzadeh H, Ebrahimzadeh F, Shekari N. Magnetic nanoparticles based dispersive micro-solid-phase extraction as a novel technique for co-extraction of acidic and basic drugs from biological fluids and waste water. J Chromatogr A. 2014;1338:1–8.

Bakırcıoğlu Y, Bakırcıoğlu D, Akman S. Biosorption of lead by filamentous fungal biomass-loaded TiO 2 nanoparticles. J HazardMater. 2010;178:1015–20.

Baytak S, Arslan Z. Solid phase extraction of trace elements in water and tissue samples on a mini column with diphenylcarbazone impregnated nano-TiO2 and their determination by inductively coupled plasma optical emission spectrometry. CLEAN- Soil Air Water. 2015;43:822–9.

Baytak S, Kasumov V. Preconcentration and determination of copper (II) by novel solid-phase extraction and high-resolution continuum source flame atomic absorption spectrometry. Anal Letters. 2017;50:105–16.

Baytak S, Mert R, Turker AR. Determination of Cu (II), Fe (III), Mn (II) and Zn (II) in various samples after preconcentration with Rhizopus oryzae loaded natural cellulose (almond bark). Intern J Environ Anal Chem. 2014;94:975–87.

Baytak S, Turker AR. The use of agrobacterium tumefaciens immobilized on Amberlite XAD-4 as a new biosorbent for the column preconcentration of iron (III), cobalt (II), manganese (II) and chromium (III). Talanta. 2005a;65:938–45.

Baytak S, Turker AR. Determination of iron (III), cobalt (II) and chromium (III) in various water samples by flame atomic absorption spectrometry after preconcentration by means of *Saccharomyces Carlsbergensis* immobilized on Amberlite XAD-4. Microchim Acta. 2005b;149:109–16.

Baytak S, Turker AR. Determination of chromium, cadmium and manganese in water and fish samples after preconcentration using Penicillium digitatum immobilized on pumice stone. CLEAN- Soil Air Water. 2009;37:314–8.

Baytak S, Zereen F, Arslan Z. Preconcentration of trace elements from water samples on a minicolumn of yeast (Yamadazyma spartinae) immobilized TiO 2 nanoparticles for determination by ICP-AES. Talanta. 2011;84:319–23.

Calero de Hoces M, Blazquez Garcia G, Ronda Galvez A. Biosorption of Cu2+ in a packed bed column by almond shell: optimization of process variables. Desalin Water Treat. 2013;51:1954–65.

Faraji M, Yamini Y, Shariati S. Application of cotton as a solid phase extraction sorbent for on-line preconcentration of copper in water samples prior to inductively coupled plasma optical emission spectrometry determination. J Hazard Mater. 2009;166:1383–8.

Hongbo X, Wanping Z, Xiaoshun Z, Jing W, Jian W. Simultaneous preconcentration of cobalt, nickel and copper in water samples by cloud point extraction method and their determination by flame atomic absorption spectrometry. Procedia Environ Sci. 2013;18:258.

Karadas C, Kara D, Fisher A. Determination of rare earth elements in seawater by inductively coupled plasma mass spectrometry with off-line column preconcentration using 2,6-diacetylpyridine functionalized Amberlite XAD-4. Anal Chim Acta. 2011;689:184–9.

Khajeh M. Application of Box–Behnken design in the optimization of a magnetic nanoparticle procedure for zinc determination in analytical samples by inductively coupled plasma optical emission spectrometry. J Hazard Mater. 2009;172:385–9.

Krawczyk M, Jeszka-Skowron M, Matusiewicz H. Sequential multi-element determination of iron and zinc in water samples by high-resolution continuum source graphite furnace atomic absorption spectrometry after column solid-phase extraction onto multiwalled carbon nanotubes. Microchem J. 2014;117:138–43.

Krishnani KK, Mengb X, Christodoulatos C, Bodduc VM. Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. J Hazard Mater. 2008; 153:1222–34.

Kumar SA, Pandey SP, Shenoy NS, Kumar SD. Matrix separation and preconcentration of rare earth elements from seawater by poly hydroxamic acid cartridge followed by determination using ICP-MS. Desalination. 2011;81:49–54.

Li S, Anderson TA, Green MJ, Maul JD, Canas-Carrell JE. Polyaromatic hydrocarbons (PAHs) sorption behaviour unaffected by the presence of multi-walled carbon nanotubes (MWNTs) in a natural soil system. Environ Sci Process Impacts. 2013;15:1130–6.

Matbouie Z, Asgharinezhad AA, Dehghani A. Solid phase extraction of cCd(II) and Pb(II) using a magnetic metal-organic framework, and their determination by FAAS. Microchim Acta. 2013;180:589–97.

Parham H, Pourreza N, Rahbar N. Solid phase extraction of lead and cadmium using solid sulfur as a new metal extractor prior to determination by flame atomic absorption spectrometry. J Hazard Mater. 2009;163:588–92.

Pereira AS, Ferreira G, Caetano L, Castro RSD, Santos AD, Padilha PM, Castro GR. 4-Amine-2-mercaptopyrimidine modified silica gel applied in Cd(II) and Pb(II) extraction from an aqueous medium. Pol J Chem. 2010;12:7–11.

Pires C, Marques AP, Guerreiro A, Magan N, Castro PM. Removal of heavy metals using different polymer matrixes as support for bacterial immobilisation. J Hazard Mater. 2011;191:277–86.

Rajfur M, Kłos A, Wacławek M. Sorption properties of algae Spirogyra sp. and their use for determination of heavy metal ions concentrations in surface water. Bio electrochemistry. 2010;80:81–6.

Sabarudin A, Lenghor AN, Oshima M, Hakim L, Takayanagi T, Gao YH, Motomizu S. Sequential-injection on-line preconcentration using chitosan resin functionalized with 2-amino-5-hydroxy benzoic acid for the determination of trace elements in environmental water samples by inductively coupled plasma-atomic emission spectrometry. Talanta. 2007;72:1609–17.

Baytak *et al. Journal of Analytical Science and Technology* (2018) 9:9

Page 6 of 6

Sahmetlioglu E, Yilmaz E, Aktas E, Soylak M. Polypyrrole/multi-walled carbon nanotube composite for the solid phase extraction of lead (II) in water samples. Talanta. 2014;119:447.

Saracoglu S, Yilmaz E, Soylak M. Speciation of chromium after coprecipitation with Cu-violuric acid and determination by flame atomic absorption spectrometry. Curr Anal Chem. 2012;8:358.

Taghizadeh M, Asgharinezhad AA, Pooladi M, Barzin M, Abbaszadeh A, Tadjarodi A. A novel magnetic metal organic framework nanocomposite for extraction and preconcentration of heavy metal ions, and its optimization via experimental design methodology. Microchim Acta. 2013;180:1073–84.

Tuzen M, Saygı KO, Usta C, Soylak M. Pseudomonas aeruginosa immobilized multiwalled carbon nanotubes as biosorbent for heavy metal ions. Bioresour Technol. 2008;99:1563–70.

Vilar VJP, Botelho CMS, Boaventura RAR. Copper removal by algae Gelidium, agar extraction algal waste and granulated algal waste: kinetics and equilibrium. Chem Engineer J. 2008;99:750–62.

Wang J, Chen C. Biosorbents for heavy metals removal and their future. Biotechnol Adv. 2009;27:195–226.

Wang J, Ma X, Fang G, Pan M, Ye X, Wang S. Preparation of iminodiacetic acid functionalized multi-walled carbon nanotubes and its application as sorbent for separation and preconcentration of heavy metal ions. J Hazard Mater. 2011;186:1985–92.

Waqar F, Jan S, Mohammad B, Hakim M, Alamb S, Yawar W. Preconcentration of rare earth elements in seawater with chelating resin having fluorinated β-diketone immobilized on styrene divinyl benzene for their determination by ICP-OES. J Chin Chem Soc. 2009;56:335–40.