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Application of 1-(2-pyridylazo)-2-naphthol-modified nanoporous silica as a technique in simultaneous trace monitoring and removal of toxic heavy metals in food and water samples

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Abstract Solid-phase extraction is one the most useful and efficient techniques for sample preparation, purification, cleanup, preconcentration, and determination of heavy metals at trace levels. In this paper, functionalized MCM-48 nanoporous silica with 1-(2-pyridylazo)-2-naphthol was applied for trace determination of copper, lead, cadmium, and nickel in water and seafood samples. The experimental conditions such as pH, sample and eluent flow rate, type, concentration and volume of the eluent, breakthrough volume, and effect of coexisting ions were optimized for efficient solid-phase extraction of trace heavy metals in different water and seafood samples. The content of solutions containing the mentioned heavy metals was determined by flame atomic absorption spectrometry (FAAS), and the limits of detection were 0.3, 0.4, 0.6, and 0.9 ng mL^{-1} for cadmium, copper, nickel, and lead, respectively. Recoveries and precisions were >98.0 and <4 %, respectively. The adsorption capacity of the modified nanoporous silica was 178 mg g^{-1} for cadmium, 110 mg g^{-1} for copper, 98 mg g^{-1} for nickel, and 210 mg g^{-1} for lead, respectively. The functionalized MCM-48 nanoporous silica with 1-(2-pyridylazo)-2-naphthol was characterized by thermogravimetry analysis (TGA), differential thermal analysis (DTA), transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FT-IR), X-ray diffraction (XRD), elemental analysis (CHN), and N_2 adsorption surface area measurement.

Keywords Heavy metals · 1-(2-Pyridylazo)-2-naphthol nanoporous silica · Water and food samples · Flame atomic absorption spectrometry

Introduction

Nowadays, the pollution caused by heavy metals in natural waters is a great concern due to potentially toxic effects on living creatures. Urbanization, industrial development, and heavy traffic lead to contamination of waters with heavy metals (Melek et al. 2006). Copper is an essential element in many biological systems which play an important role in carbohydrate and lipid metabolisms. In general, copper with nearly 40 μg L^{-1} is required for normal metabolism of many living organisms; however, at higher levels, it is considered to be toxic and severe intoxication will mainly affect the blood and kidneys (Tabrizi 2007). Cadmium is also one of the most hazardous elements to human health because it can cause adverse effects on metabolic processes of human beings (Gama et al. 2006). Cadmium is highly toxic even at low concentrations and can cause serious damages to body organs such as kidney, liver, and lung (Maranho et al. 2005). Nickel among the first row of transition metals is a moderately toxic element,

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and the inhalation of this metal and its compounds can lead to serious problems including the cancer of respiratory system (Ferreira et al. 2001). Finally, the toxicity of lead which widely exists in the environment is worth mentioning. This metal can accumulate in the vital organs of human and animals, and its cumulative poisoning effects can cause serious hematological damages such as brain damage, anemia, and kidney malfunctioning. Lead concentration in natural waters is typically between 2 and 10 ng mL^{-1} for which the upper limit recommended by World Health Organization is less than 10 ng mL^{-1} (Mayer and Wilson 1998). Determination of trace heavy metals constitutes one of the most important topics in analytical chemistry (Behbahani et al. 2013a, 2014a; Salarian et al. 2014; Kalate Bojdi et al. 2014; Behbahani et al. 2014b). This topic is also applied in different areas such as biology and medicine (da Silva et al. 2004). However, the level of heavy metal concentration in environmental samples is fairly low and preconcentration procedures are often required (Duran et al. 2009). Among numbers of methods such as liquid-liquid extraction (Komjarova and Blust 2006; Wei et al. 2003; Behbahani et al. 2014c), chemical precipitation (Matlock et al. 2002a, 2002b), ion exchange (Akcin et al. 2011), reverse osmosis adsorption (Akieh et al. 2008), and solid-phase extraction (SPE), solid-phase extraction has attracted a considerable amount of interests for the preconcentration of toxic heavy metals (Tuzen et al. 2008; Behbahani et al. 2014d, 2014e, 2014f, 2014g; Ghaedi et al. 2008, 2007), due to higher efficiency and low consumption of pure organic solvents. This method is simple, efficient, selective, cost-effective, and it is easy to automate without need for emulsion, and it is also safe, regarding to the reagents that has employed (Nabid et al. 2014). According to the nature of this method, the key point is choosing the appropriate adsorbent, since this factor could affect selectivity and sensitivity of the method (Behbahani et al. 2014h). With the emergence of SPE, various sorbents have been developed such as carbon nanotubes (Behbahani et al. 2014i), activated carbon (Starvin and Prasada Rao 2004), polymeric adsorbent resin (Huck and Bonn 2000), Amberlite XAD-7 resin (Kumar et al. 2001), synthetic zeolites (Mostafavi et al. 2006), modified chromosorb (Tuzen and Soylak 2006), TiO_2 (Behbahani et al. 2013b), activated alumina (Poole 2003), and nanoporous silica (Bagheri et al. 2012). Among these sorbents, nanoporous silicas such as MCM-41, MCM-4, and SBA-15 have attracted great attention because of their good mechanical and thermal stability and their lower susceptibility to swelling and shrinking (Mehrani et al. 2011). In spite of these advantages, their applications without proper surface modifications and functionalizations are limited (Behbahani et al. 2014j). Furthermore, properties of these materials depend on the functional groups that have been anchored to the surface of nanoporous silica. Among lots of suitable ligands in coordination chemistry, 1-(2-pyridylazo)-2-naphthol is a well-known ligand for coordinating to transition metals in general and cadmium, lead, nickel, and copper in particular.

In this paper, MCM-48 nanoporous silica was functionalized with 1-(2-pyridylazo)-2-naphthol (PAN) and utilized as an adsorbent for simultaneous separation of ultra-trace amounts of cadmium, copper, nickel, and lead ions. Various factors affecting the adsorption and desorption steps for these heavy metals were investigated and optimized. The studied factors include effects of pH, sample and eluent flow rate, type, concentration and volume of the eluent for elution of the heavy metals, breakthrough volume, and effect of coexisting ions on the separation and determination of the heavy metals. The PAN-functionalized nanoporous silica (PAN-MCM-48) was successfully applied for solid-phase extraction of lead, copper, cadmium, and nickel in water samples, and flame atomic absorption spectrometry (FAAS) was used to measure the above ions in solutions. The developed method was applied for determination of cadmium, copper, nickel, and lead ions in several water and seafood samples, and the accuracy of the method was confirmed by two standard materials.

Experimental

Reagents and materials

Sodium nitrite, 4-nitrobenzaldehyde, PAN, and sodium hydrosulfite were purchased from Aldrich Company. All other reagents used in this study (solvents, acids, 3-amino-propyltriethoxysilane, and stock solutions of metal ions) were of analytical grade and purchased from Merck Chemical Company (Darmstadt, Germany, www.merck.de). Colloidal silica with particle size below 0.5 mm and surface area of 200 m^2/g was purchased from Merck and used immediately. Double-distilled water from a Milli-Q purification system

(Millipore, Bedford, MA, USA) was used for the preparation of solutions. A stock solution (2.0 mg mL^{-1}) of cadmium, copper, nickel, and lead ions was prepared by dissolving an appropriate amount of corresponding nitrate salts in double-distilled water. Soil (NCS DC 73323) and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326) from Bulgaria was prepared as the reference materials.

Apparatus

Cadmium, copper, nickel, and lead concentration was determined by an AA-680 Shimadzu (Kyoto, Japan) FAAS in an air-acetylene flame, according to the user's manual provided by the manufacturer. Cadmium, copper, nickel, and lead hollow cathode lamps (HCLs) were used as the radiation source with wavelengths of 228.8, 324.8, 232, and 283 nm, respectively. The pH was measured at 25±1 °C with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. A peristaltic pump was obtained from Leybold (Cologne, Germany) and an adjustable vacuum gauge and controller were obtained from Analytichem International (Harber City, CA). The adjustable vacuum gauge allowed the control of the flow rate during the extraction. The CHN analysis was performed on a Thermo Finnigan Flash EA112 elemental analyzer (Okehampton, UK). The specific surface areas were measured by nitrogen adsorption technique using a Micromeritics ASPS 2010 analyzer. IR spectra were recorded on a Bruker IFS-66 FT-IR spectrophotometer. The transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100F field emission transmission electron microscope. Low-angle X-ray diffraction patterns were obtained on a Philips-PW 17C diffractometer with Cu K_α radiation. Thermogravimetry and differential scanning calorimetry (TGA/DSC) were carried out on a Bahr STA-503 instrument under air atmosphere.

Preparation of PAN-MCM-48 and PAN-SiO_2

MCM-48 nanoporous silica was prepared according to the earlier report (Xu et al. 1998) and modified with amine group according to the published procedure (Johnson and Stein 2001). Briefly, 1.0 g of MCM-48 was suspended in 50 mL of toluene and then 3-aminopropyltriethoxysilane (2.0 mL) was added to the mixture and was refluxed for 24 h under N_2 atmosphere. The resulted solid was suspended in 100 mL of toluene, and an excess amount of 4-nitrobenzaldehyde (5.0 g) was added to the mixture. After refluxing the mixture for 24 h, the solid was removed from the solvent by filtration and suspended in 50 mL of water containing 5.0 g of sodium hydrosulfite. The resulted solid was filtrated, washed with water, and suspended in 50 mL of aqueous solution of acetic acid (1 %) in ice bath. Then, a total amount of 2.0 g of sodium nitrite was added to the mixture and stirred overnight. The solid was removed by filtration and again suspended in 50 mL of ethanol, and then 0.50 g of PAN was added to the mixture in ice bath. After stirring the mixture for 24 h, light red solid was separated by filtration and washed several times with ethanol and water. The synthesis of PAN-MCM-48 was confirmed by IR spectroscopy, low-angle X-ray diffraction, elemental and thermal analysis, and N_2 adsorption surface area measurement.

PAN-functionalized SiO_2 was prepared similarly as described for the PAN-MCM-48.

Water samples for heavy metal analysis

The method was successfully used in the determination of cadmium, copper, nickel, and lead in distilled, tap, river, lake, sea, and waste water samples. The polyethylene bottles filled with the samples were cleaned with detergent, water, diluted nitric acid, and water in sequence. The samples were immediately filtered through a cellulose filter membrane (pore size 0.45 μm) and were acidified to pH of 2.0 for storage. Tap water samples were taken from our research laboratory without pretreatment. Before determination, the samples were adjusted to pH of 6.0 according to optimized experimental conditions.

Results and discussion

Sorbent characterization

The MCM-48 nanoporous silica was synthesized according to the earlier report by the hydrothermal method. The formation of MCM-48 was confirmed by low-angle X-ray powder diffraction and nitrogen adsorption analysis. The N_2 adsorption analysis showed the surface area of 1026 m^2 g^{-1} for the nanoporous silica which indicates that the material has a nanopore structure. After functionalization of the MCM-48 with 3-

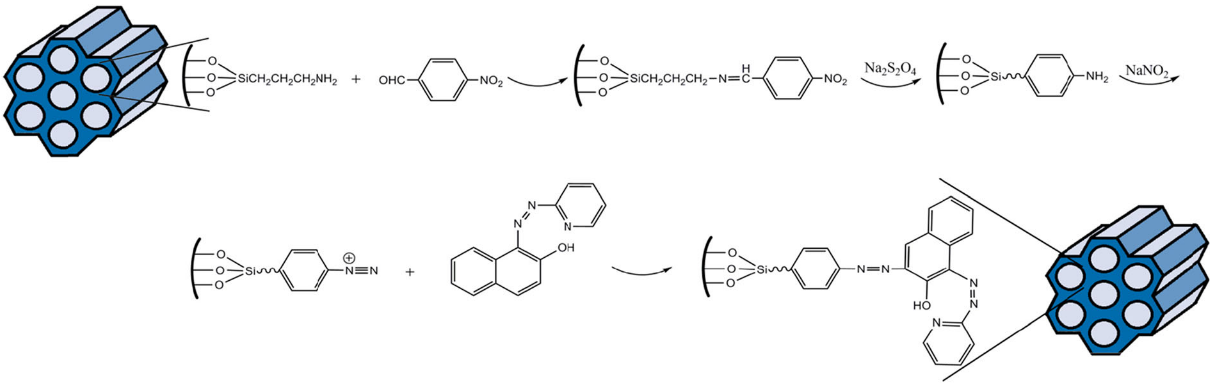
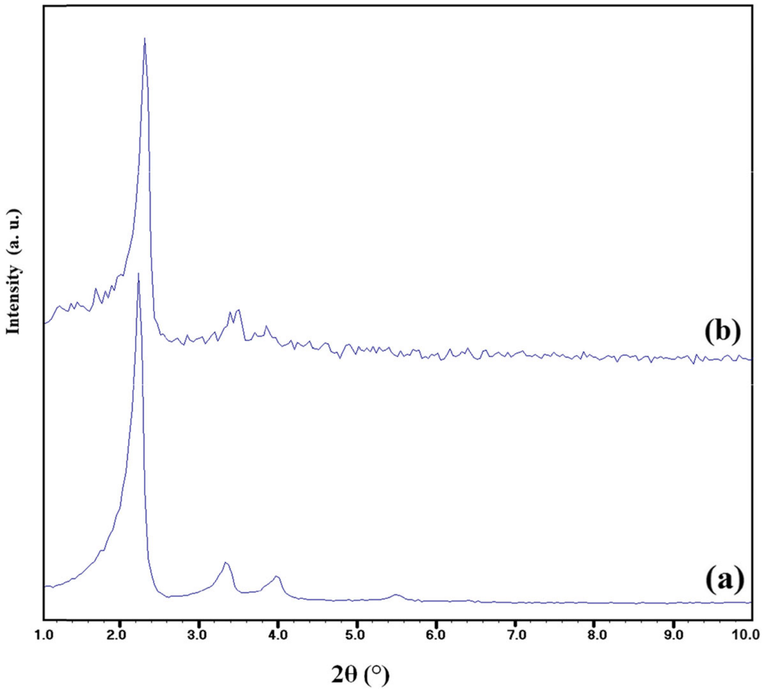


Fig. 1 A scheme for modifying MCM-48 with 1-(2-pyridylazo)-2-naphthol

aminopropyltriethoxysilane agent, the amine-functionalized material was reacted with the aldehyde group of 4-nitrobenzaldehyde. This reaction led to the formation of the nitro-functionalized MCM-48 (Fig. 1). The subsequent reactions which resulted in the formation of PAN-modified MCM-48 was carried out according to previous report (Liu et al. 1995). Formation of PAN-MCM-48 nanoporous silica was confirmed by IR spectroscopy, low-angle X-ray diffraction, elemental and thermal analysis, and N_2 adsorption surface area measurement. The FT-IR spectra of PAN-MCM-48 showed stretching vibration bands of PAN at 1608 cm^{-1} (N=N), 1598 cm^{-1} (C–C aromatic ring), 1281 cm^{-1} (C–N), 2983 cm^{-1} (aliphatic C–H), and 3027 cm^{-1} (aromatic C–H) and confirmed the presence of PAN groups in the sorbent. Elemental analysis of the PAN-functionalized MCM-48 showed 0.86 mmol g^{-1} of PAN in the sorbent. According to the N_2 adsorption results and decrease of the surface area from 1026 to 574 m^2 g^{-1} after functionalization, PAN is mainly grafted within the channels of nanoporous MCM-48. The low-angle X-ray diffraction pattern of PAN-MCM-48 showed slight shifts in peaks and decrease in intensity in comparison to unfunctionalized MCM-48 (Fig. 2). According to this pattern, the nanopore structure of MCM-48 remains intact after functionalization.

Fig. 2 The low-angle X-ray diffraction patterns of MCM-48 (**a**) and 1-(2-pyridylazo)-2-naphthol-MCM-48 (**b**)



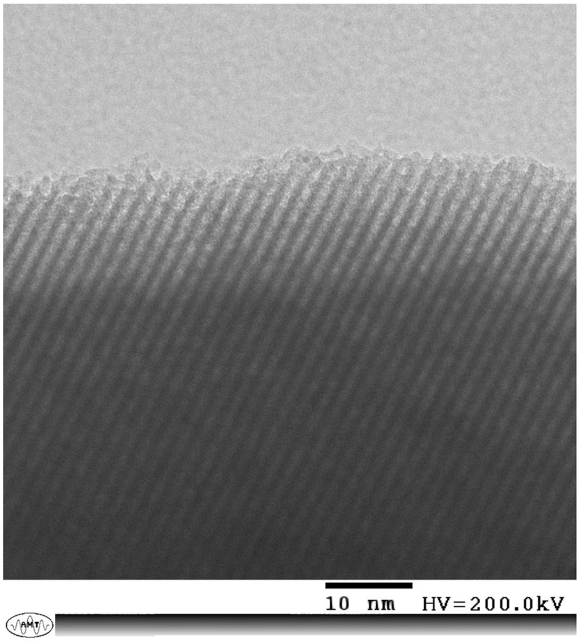


Fig. 3 TEM micrograph of 1-(2-pyridylazo)-2-naphthol-modified MCM-48

For further investigation of the nanostructure of the sorbent which is a key point in its efficiency, the TEM study was carried out and the result also confirmed that the nanopore structure of the MCM-48 has been retained after functionalization. The pores, bright spots, the walls, and dark spots are clearly visible from TEM micrograph in Fig. 3. The thermal stability of PAN-MCM-48 has been investigated by TGA/DSC analysis. According to the TGA/DSC analysis, sorbent is stable up to 160 °C. Moreover, about 37 % of loss weigh is in good agreement with the elemental analysis results about PAN concentration (Fig. 4).

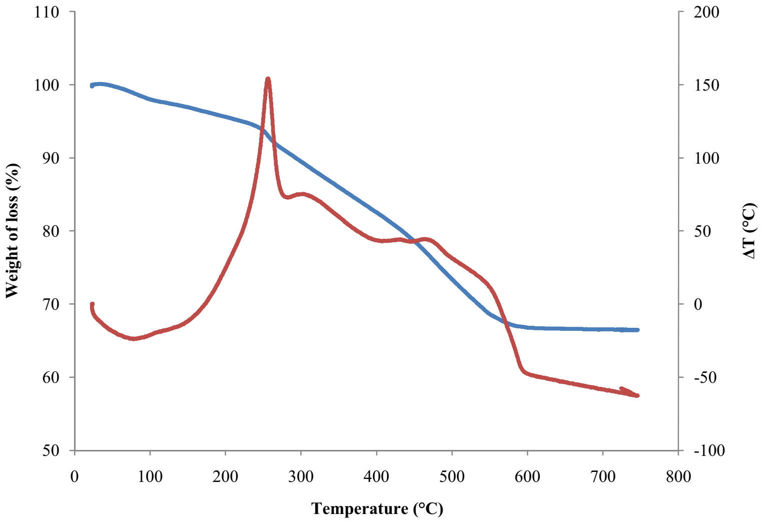
Column preparation

PAN-MCM-48 (100 mg) was packed in a glass column with dimensions of 120 mm in length and 20 mm in diameter and blocked by two polypropylene filters at the ends to prevent the loss of the nanoporous material during sample loading. Prior to extraction, the column was preconditioned successively with 5 mL of absolute ethanol, 5 mL of toluene, and 5 mL of absolute ethanol, and then it was washed with double-distilled water until it became free of organic solvents. The column was dried in a vacuum oven at 60 °C for 3 h, and it was used in the following optimization conditions.

Optimization of the retention conditions

Among the tested variables, pH was found to be the most critical parameter for adsorption of metals on the nanoporous silica. To evaluate the effect of pH on the retention efficiency, the pH of 25 mL of sample solution containing 2 mg L^{-1} of cadmium, copper, nickel, and lead ions was adjusted to fit in the range of 2–8. As can be seen in Fig. 5, the quantitative retention of cadmium, copper, nickel, and lead ions on the PAN-MCM-48 was obtained in the pH of 6.0. Lowering the pH value of the solution decreased the quantitative recovery of the sorbent due to the electrostatic repulsion of the protonated

Fig. 4 TGA/DSC analysis of 1-(2-pyridylazo)-2-naphthol-modified MCM-48



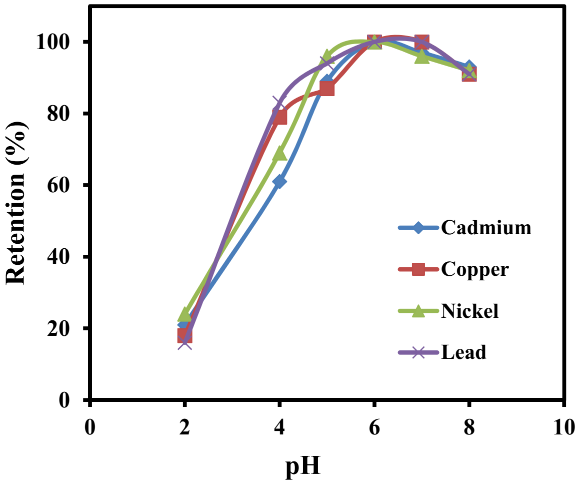


Fig. 5 Effect of pH of sample solutions on retention of cadmium, copper, nickel, and lead ions by 1-(2-pyridylazo)-2-naphthol-MCM-48. Conditions: sample concentration, 2 µg mL^{-1}; sample volume, 25 mL

active sites on the sorbent with the positively charged cadmium, copper, nickel, and lead species. Due to hydrolysis, pH above 8.0 was not tested.

To optimize the sample flow rate, 25-mL solutions of 2 mg L^{-1} cadmium, copper, nickel, and lead ions were adjusted to pH of 6.0 and then passed through the column at flow rates in the range of 1–18 mL min^{-1} with a peristaltic pump. The results in Fig. 6 demonstrated that the sample flow rate variation in the ranges of 1–15 mL min^{-1} had no effect on the retention of the heavy metals on PAN-MCM-48.

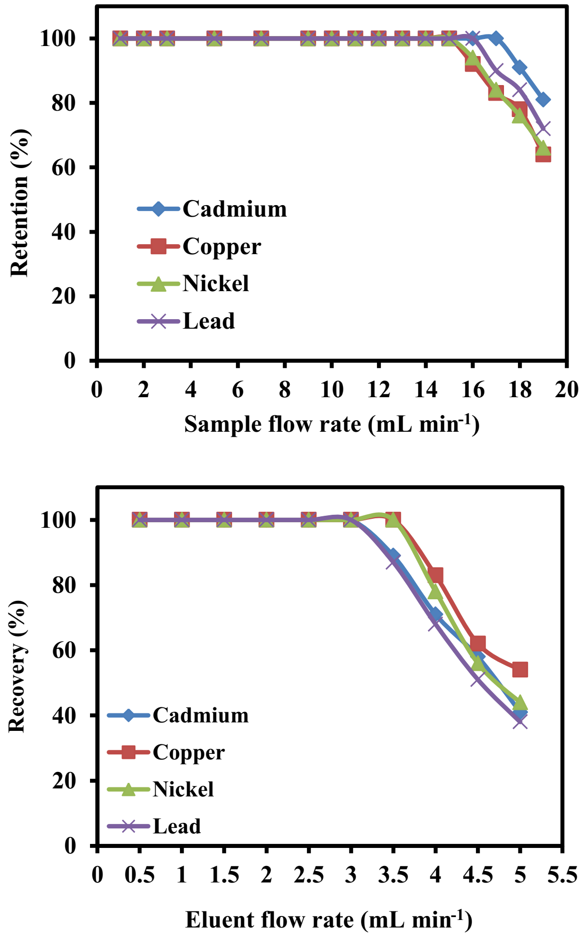


Fig. 6 The effect of sample (**a**) and eluent (**b**) flow rate on the retention and recovery of heavy metals (Cd, Pb, Ni, and Cu)

Optimization of the elution conditions

For desorption of cadmium, copper, nickel, and lead ions from PAN-functionalized nanoporous silica, a series of selected eluents, such as HNO_3, HCl, and CH_3COOH at different concentrations were used. As shown in Table 1, it was eventually found that HCl:HNO_3 (1:1 (mol L^{-1})) provided an effective elution of cadmium, copper, nickel, and lead ions from PAN-functionalized nanoporous silica. The effect of eluent volume on the recovery of the heavy metals was also studied. As shown in Table 1, quantitative recovery could be obtained with 5 mL of HCl:HNO_3 (1:1 (mol L^{-1})). Therefore, volumes of 5 mL of eluent for desorption of cadmium, copper, nickel, and lead ions were used in the remaining experiments. The influence of the eluent flow rate on metals recovery was also studied. The results in Fig. 6 demonstrated that the quantitative recoveries for cadmium, copper, nickel, and lead ions were obtained at a flow rate range of 0.5–3.0 mL min^{-1} with HCl:HNO_3 (1:1 (mol L^{-1})).

Effect of the volume of sample solutions

A higher preconcentration factor can be obtained by increasing the sample to eluent volume ratio by either decreasing the eluent volume and/or increasing the sample volume. Therefore, the maximum volume of sample solution was investigated by increasing the volume of metal ion solution with a constant amount of ions (0.1 mg of cadmium, copper, nickel, and lead ions). Sample solution volumes of 50, 100, 300, 500, 600, 1000, 1200, 1300, 1400, 1500, 1600, 1700, and 1800 mL containing cadmium, copper, nickel, and lead ions were passed through the column. The results (Fig. 7) demonstrated that the dilution effect was not

Table 1 Effect of type, concentration, and volume of eluent on extraction efficiency

Eluent	Concentration (mol L^{-1})	Volume (mL)	R^a %±S_b			
			Copper	Lead	Cadmium	Nickel
HNO_3	4	10	84.0±2.0	97.0±1.0	96.0±1.0	74.0±2.0
HCl	4	10	88.0±1.0	97.0±2.0	97.0±1.0	78.0±2.0
CH_3COOH	4	10	44.0±1.0	66.0±1.0	74.0±1.0	68.0±2.0
$HCl:CH_3COOH$	2:2	10	67.0±1.0	82.0±2.0	89.0±1.0	62.0±1.0
$HNO_3:CH_3COOH$	2:2	10	51.0±2.0	78.0±1.0	81.0±2.0	54.0±2.0
$HNO_3:HCl$	1:3	10	99.0±1.0	99.0±1.0	99.0±1.0	99.0±1.0
$HNO_3:HCl$	3:1	10	98.0±0.2	99.0±1.0	99.0±1.0	99.0±1.0
$HNO_3:HCl$	2:1	10	99.0±1.0	99.0±1.0	98.0±2.0	99.0±1.0
$HNO_3:HCl$	1:2	10	99.0±1.0	99.0±1.0	99.0±1.0	99.0±1.0
$HNO_3:HCl$	1:1	10	99.0±1.0	99.0±1.0	99.0±1.0	99.0±1.0
$HNO_3:HCl$	1:0.5	10	94.0±2.0	96.0±1.0	93.0±1.0	92.0±2.0
$HNO_3:HCl$	0.5:1	10	95.0±2.0	98.0±1.0	96.0±1.0	94.0±2.0
$HNO_3:HCl$	1:1	7.5	99.0±1.0	99.0±1.0	99.0±1.0	99.0±1.0
$HNO_3:HCl$	1:1	5	99.0±1.0	99.0±1.0	99.0±1.0	99.0±1.0
$HNO_3:HCl$	1:1	2.5	79.0±1.0	74.0±1.0	68.0±1.0	72.0±1.0

[a] Recovery

[b] Standard deviation

significant for sample volumes of 1400 mL for cadmium, 1600 mL for copper, 1500 mL for nickel, and 1400 mL for lead ions on PAN-MCM-48. It was found that the simultaneous quantitative recovery of cadmium, copper, nickel, and lead ions on PAN-MCM-48 can be obtained for sample volume up to 1400 mL.

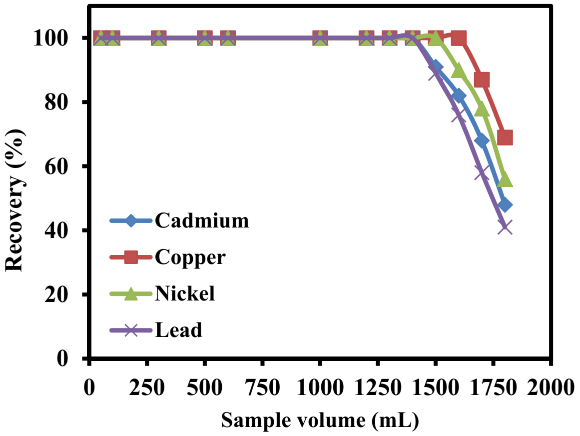


Fig. 7 Effect of sample solution volume on extraction recovery of cadmium, copper, nickel, and lead ions on 1-(2-pyridylazo)-2-naphthol-MCM-48. Condition: 0.1 mg of cadmium and copper ions; solution pH, 6; sample flow rate, 15 mL min^{-1}; eluent, 5 mL of HCl:HNO3 (1:1 (mol L^{-1})); eluent flow rate, 3 mL min^{-1}

Effect of the interfering ions

To investigate the effect of various cations found in natural samples, elements that are known as alkaline, alkaline earth, and transition metals were added to 100 mL of solution containing 0.01 mg of cadmium, 0.01 mg of copper, 0.01 mg of nickel, and 0.01 mg of lead ions. The degree of tolerance for some alkaline, alkaline earth, and transition metal ions are presented in Table 2. From the tolerance data, it can be seen that the foreign ions have no significant effects on preconcentration of cadmium, copper, nickel, and lead ions at pH of 6.0.

Adsorption capacity

The adsorption capacity of PAN-MCM-48 for cadmium, copper, nickel, and lead ions was studied by passing 500-mL portions of aqueous solutions containing 25 mg of cadmium, copper, nickel, and lead ions through the column at optimal pH. In order to evaluate the maximum adsorption capacity, the difference between the concentration of the solution before passing through the column and the concentration of the solution after passing through the column was calculated. The

Table 2 The tolerance limit of various ions on the determination of cadmium, lead, nickel, and copper ions

External ion	Tolerable concentration ratio X/Cd, Cu, Ni, Pb	R[a] %±S_b			
		Cadmium	Copper	Nickel	Lead
K^+	10,000	99.0±1.0	99.0±1.0	99.0±1.0	99.0±1.0
Na^+	10,000	99.0±2.0	99.0±2.0	99.0±2.0	99.0±1.0
Cs^+	10,000	99.0±2.0	98.0±1.0	98.0±1.0	98.0±2.0
Ca^{2+}	1000	98.0±2.0	97.0±2.0	97.0±1.0	98.0±1.0
Mg^{2+}	900	96.0±1.0	98.0±2.0	99.0±1.0	98.0±1.0
Al^{3+}	1000	98.0±2.0	97.0±1.0	98.0±1.0	96.0±2.0
Cr^{3+}	900	97.0±1.0	96.0±2.0	97.0±2.0	96.0±1.0
Fe^{2+}	800	96.0±1.0	97.0±2.0	98.0±1.0	98.0±1.0
Mn^{2+}	900	99.0±1.0	97.0±1.0	96.0±1.0	98.0±2.0
CrO_4^{2-}	1000	98.0±1.0	97.0±1.0	98.0±1.0	97.0±1.0
PO_4^{3-}	1000	98.0±1.0	97.0±2.0	96.0±1.0	97.0±1.0

Conditions: sample pH, 6; sample volume, 100 mL; 0.01 mg of cadmium, lead, nickel, and copper ions; sample flow rate, 15 mL min^{-1}; eluent, 5 mL of HCl:HNO3 (1:1 (mol L^{-1})); eluent flow rate, 3 mL min^{-1}

X concentration of diverse ions

[a] Recovery

[b] Standard deviation

obtained capacities of PAN-MCM-48 were found to be 178, 110, 98, and 210 mg g^{-1} for cadmium, copper, nickel, and lead ions, respectively.

Analytical performance

Under the optimized conditions, calibration curves were sketched for the determination of cadmium, copper, nickel, and lead ions according to the general procedure. Linearity was maintained 1–100 ng mL^{-1} for cadmium, 1–110 ng mL^{-1} for copper, 1–110 ng mL^{-1} for nickel, and 2–110 ng mL^{-1} for lead in initial solution. The correlation of determination (r^2) was 0.997 for cadmium, 0.996 for copper, 0.997 for nickel, and 0.998 for lead ions. The limit of detection which is defined as $C_{LOD}=3S_b/m$, where S_b is the standard deviation of ten replicate blank signals and m is the slope of the calibration curve after preconcentration, for a sample volume of 500 mL, was found to be 0.3 ng mL^{-1} for cadmium, 0.4 ng mL^{-1} for copper, 0.6 ng mL^{-1} for nickel, and 0.9 ng mL^{-1} for lead ions, respectively. The relative standard deviations for eight separate column experiments for determination of 5.0 μg of cadmium, copper, nickel, and lead ions in 100 mL of water was 3.2, 3.2, 3.1, and 3.6 %, respectively.

Table 3 The effect of nanopores on the analytical performance of the sorbent

Adsorbent	Adsorption capacity (mg g^{-1})				Sample flow rate (mL min^{-1})	Sample volume (mL min^{-1})
	Cd	Cu	Pb	Ni		
PAN-functionalized MCM-48	178	110	210	98	1–15	1400
PAN-immobilized silica	32	21	48	18	1–4	300

Effect of nanopores on the analytical performance

To study the effect of pores on the analytical performance, the adsorption capacity, sample flow rate, and sample volume of nanoporous was compared to synthesized diphenylcarbazide-modified SiO_2. As results shown in Table 3, the pores caused this sorbent to

Table 4 Determination of cadmium, lead, nickel, and copper recovery in certified reference materials

Sample	Element	Concentration (mg kg^{-1})		Relative error (%)
		Certified	Found	
Ore polymetallic gold Zidarovo PMZrZ (206 BG 326)	Cd	212	206	−2.8
	Pb	5.47	5.34	−2.4
	Ni	12	11.6	−3.3
	Cu	0.51	0.50	−1.9
Soil (NCS DC 73323)	Cd	0.45	0.43	−4.4
	Pb	552	538	−2.5
	Ni	40	39.2	−2.0
	Cu	144	140	−2.8

Table 5 Analysis of cadmium, lead, nickel, and copper in various water samples

Sample	Element	Real sample (ng mL^{-1})	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Lake water	Cd	1.10	5.00	6.20	101.6
	Cu	11.20	5.00	16.10	99.3
	Pb	7.80	5.00	12.60	98.4
	Ni	64.10	5.00	69.20	100.1
Sea water	Cd	1.60	5.00	6.50	98.5
	Cu	54.40	5.00	59.20	99.6
	Pb	3.90	5.00	9.00	101.1
	Ni	64.10	5.00	69.15	100.07
Waste water	Cd	3.20	5.00	8.10	98.8
	Cu	19.80	5.00	24.60	99.2
	Pb	10.40	5.00	15.30	99.3
	Ni	34.70	5.00	39.50	99.4
Sample	Element	Real sample (μg kg^{-1})	Added (μg kg^{-1})	Found (μg kg^{-1})	Recovery (%)
Shrimp	Cd	5.8	10.0	15.6	98.7
	Cu	90.2	10.0	99.8	99.6
	Pb	31.8	10.0	41.5	99.2
	Ni	42.1	10.0	51.9	99.6
Crab	Cd	6.1	10.0	15.9	98.7
	Cu	89.5	10.0	99.2	99.6
	Pb	37.4	10.0	46.9	98.9
	Ni	24.2	10.0	33.9	99.1
Fish	Cd	3.6	10.0	13.4	98.5
	Cu	84.2	10.0	93.9	99.6
	Pb	29.8	10.0	39.5	99.2
	Ni	31.2	10.0	40.9	99.2

become very valuable for separation and preconcentration of metal ions.

Validation of the method

The concentration of cadmium, copper, nickel, and lead ions obtained by PAN-MCM-48 was compared to the standard materials. For this reason, the concentration of the heavy metal ions was determined at optimum conditions in standard reference materials (soil (NCS DC 73323)) and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326)). As it can be seen in Table 4, good correlation was achieved between estimated content by the present method and reference materials. To digest the certified reference materials, 50 mg from each of them was digested with 6 mL of HCl (37 %) and 2 mL of HNO_3 (65 %) in a microwave digestion system. The digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W, and then venting for 8 min. Then, the resulted solution from digestion was diluted to 500 mL with deionized water before adjusting the pH to 6.0. Therefore, PAN-MCM-48 can be used as a reliable solid phase for extraction and determination of cadmium, copper, nickel, and lead ions in environmental samples.

Determination of cadmium, copper, nickel, and lead in real samples

Since natural samples have complex matrices, nonspecific background absorption was caused by interfering species of the sample matrix. To reduce this undesirable effect, nanoporous silica was applied for selective extraction of cadmium, copper, nickel, and lead ions in pH of 6.0. Tables 5 shows the cadmium, copper, nickel, and lead ion recoveries in various water and food samples.

Table 6 A comparison between the proposed solid-phase extraction method and previous works

Instrument	Method	Elements	LOD (ng mL^{-1})	PF	MAC (mg g^{-1})	Reference
FAAS	1,8-Diaminonaphthalene/multiwalled carbon nanotubes-COOH	Lead	0.7	400	175.2	Nabid et al. (2014)
		Cadmium	0.09	400	101.2	
		Copper	–	–	–	
		Nickel	–	–	–	
FAAS	Amine-functionalized graphene nanosheet	Lead	1.0	320	210	Behbahani et al. (2014g)
		Cadmium	0.03	320	178	
		Copper	0.05	320	142	
		Nickel	0.2	320	110	
FAAS	Dithizone-SBA-15	Lead	0.45	–	208	Behbahani et al. (2013c)
		Cadmium	0.09	–	189	
		Copper	0.16	–	102	
		Nickel	0.21	28	91	
FAAS	Tetragonal star-like polyaniline nanostructures	Lead	0.9	280	110	Behbahani et al. (2014d)
		Cadmium	–	–	–	
		Copper	0.4	280	84	
		Nickel	–	–	–	
FAAS	Proposed method	Lead	0.9	280	210	–
		Cadmium	0.3	280	178	
		Copper	0.4	280	110	
		Nickel	0.6	280	98	

PF preconcentration factor, *MAC* maximum adsorption capacity

Table 6 provide a comparison between the proposed method and other previous works.

Conclusion

In the present study, an application of PAN-MCM-48 was introduced in the area of solid-phase extraction. The nanoporous structure of PAN-MCM-48 can cause the fast adsorption of lead, copper, cadmium, and nickel. The affecting parameters on adsorption and desorption steps were evaluated and optimized. Determination of the heavy metals resulted in good quantitative recoveries in water samples. Under the optimized experimental conditions, the detection limits of present method for the determination of lead, cadmium, nickel, and copper ions were 0.9, 0.3, 0.6, and 0.4 ng mL^{-1}, respectively. The recoveries for these elements were very satisfactory. In addition, PAN-MCM-48 showed high tolerance to interferences from the matrix ions, and finally, the important features of the proposed method were its high adsorption capacity, good preconcentration factor, and low detection limit which is distinctive among other solid-phase extraction methods (Nabid et al. 2014; Behbahani et al. 2013c, 2014d, 2014g). The proposed method was applicable to the determination of trace amount of these heavy metals in real water and food samples.

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