

Solid Phase Extraction of Pb(II) and Cd(II) in Food, Soil, and Water Samples Based on 1-(2-Pyridylazo)-2-Naphthol-Functionalized Organic–Inorganic Mesoporous Material with the aid of Experimental Design Methodology

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Abstract An effective sorbent of 1-(2-Pyridylazo)-2-naphthol-functionalized mesoporous silica has been prepared to simultaneous separation and preconcentration of lead and cadmium ions in aqueous solution. Structural characterization of 1-(2-Pyridylazo)-2-naphthol-functionalized organic–inorganic hybrid mesoporous materials was conducted by Fourier transform infrared spectroscopy, transmission electron microscopy, N₂ adsorption–desorption measurement, X-ray diffraction, and elemental and thermal analysis, which confirmed the successful grafting of organic moiety on mesoporous silica. The affecting parameters on adsorption and desorption steps were optimized by Box-Behnken design through response surface methodology. Three variables (pH value, sorption time, and amount of the sorbent) were selected as the main factors affecting sorption step, while four variables (type of eluent, eluent volume, eluent concentration, and elution time) were selected for desorption step in the optimization study. The optimized values by this optimization method were 10 mg, 8 min, 6.3, HCl, 1.6 mL, 1.2 mol L⁻¹ HCl, and 10 min, for amount of sorbent, sorption time, pH of solution, type, volume, and concentration of the eluent, and elution time, respectively. Under the optimized conditions, the detection limits of the proposed method for lead and cadmium ions were found to be 0.9 and 0.04 µg L⁻¹, respectively, while the relative standard deviation (RSD) for five replicate measurements was calculated to be <3 % for both ions. For proving that the proposed method is reliable, a wide range of food, soil,

and water samples with different and complex matrixes was used.

Keywords Cadmium and lead ions · Solid phase extraction · Response surface methodology · Organic–inorganic hybrid mesoporous materials

Introduction

Heavy metals like Cd(II) and Pb(II) are considered as dangerous toxic element to the environment and human health. The main sources of metal contamination are industrial development and human activities (Carbonell-Barrachina et al. 2002; Behbahani et al. 2014a; Bagheri et al. 2012a; Bagheri et al. 2012b). However, these heavy metals are entered into the human body by ingestion of contaminated food, air, and water, to create the vulnerability of vital organs of the human body such as liver, kidney tissues and brain (Chen and Teo 2001; Kazi et al. 2008; Duran et al. 2013; Behbahani et al. 2014b).

Sample preparation is one of the most important and critical step in analytical chemistry. A number of preconcentration methods, including cold-induced aggregation microextraction (Baghdadi and Shemirani 2008), head space liquid phase microextraction (Zhang and Lee 2010), in situ solvent formation microextraction (Galan-Cano et al. 2012), dispersive liquid-liquid microextraction (DLLME) (Asadollahzadeh et al. 2014; Tsenga et al. 2014; Soylak and Tuzen 2006; Duran et al. 2008; Soylak et al. 2003), solid phase extraction (SPE) (Sahmetlioglu et al. 2014; Behbahani et al. 2013a), and magnetic solid phase extraction (MSPE) (Bagheri et al. 2012c) have been widely used for preconcentration and detection of organic and inorganic analytes.

Among these techniques, SPE offers an excellent alternative to the conventional sample preparation methods because

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of its simplicity, consumption of small volumes of organic solvent, and ability to achieve a higher enrichment factor and sensitivity.

Mesoporous solids have been widely used in different fields such as catalysis and sorption materials because of their large surface area, high porosity, controlled morphology, and easy functionalization (Feng et al. 1997; Fryxell 2006). Specific syntheses and applications for the mesoporous materials have been increasing in recent years. They are widely applied in environmental treatment techniques especially because of their high sorption capacity and good dispersibility in aqueous solutions (Liu et al. 2000; Mureseanu et al. 2008; Wang et al. 2005; Gao et al. 2007; Zhang et al. 2007). Functionalized mesoporous materials have been used for the sorption of metals such as Cu(II) (Jeong et al. 2011), Hg(II) (Mureseanu et al. 2010), Pb(II) (Hajiaghbabaei et al. 2011), Zn(II) (Dong et al. 2010), and Ag(I) (Ebrahimzadeh et al. 2010).

One major challenge in the utilization of extraction techniques is the selection of experimental conditions which can provide acceptable response at low analyte concentration. Chemometrics, a term originally coined by Wold in 1971 (Brereton 1990), is “a chemical discipline that uses mathematics, statistics, and formal logic; (I) to design or select optimal experimental procedures; (II) to provide maximum relevant chemical information by analyzing chemical data; and (III) to obtain knowledge about chemical systems”. Moreover, chemometrics tools through the development of mathematical models can assess the statistical significance of the independent variable effects being investigated as well as evaluate their interaction effects. If significant interaction effects between the examined variables exist, the optimal conditions indicated by the univariate studies will be much different from the correct results of the multivariate optimization (Ferreira et al. 2007). Box-Behnken design (BBD) is an efficient option (three-level factor quadratic design) at which the experimental points are located on the midpoints of the edges of a cube and at the center (central points). The special arrangement of the BBD levels allows the number of design points to increase at the same rate as the number of polynomial coefficients. The spherical nature of the BBD combined with the fact that the design is rotatable or nearly rotatable suggests that ample center runs should be used (Stalikas et al. 2009). An advantage of BBD is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. Therefore, these designs are useful in avoiding experiments that would be performed under extreme conditions, for which unsatisfactory results might occur (Teixeira Tarley et al. 2009).

The primary aim of the current work is to synthesize an absorbent by modifying MCM-48 with 1-(2-Pyridylazo)-2-naphthol. The newly modified mesoporous material was employed in solid phase extraction for the extraction and

preconcentration of lead and cadmium ions. Structural characterization of 1-(2-Pyridylazo)-2-naphthol-functionalized organic–inorganic hybrid mesoporous materials was conducted by Fourier transform infrared spectroscopy, transmission electron microscopy, N₂ adsorption–desorption measurement, X-ray diffraction, and elemental and thermal analysis, which confirmed the successful grafting of organic moiety on mesoporous silica. BBD was used to optimize the influence of factors in adsorption and desorption steps, separately. Finally, the introduced solid phase extraction technique was successfully applied for the extraction and preconcentration of lead and cadmium ions in soil and water samples.

Experimental

Apparatus

Lead and cadmium concentration was determined by an AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (FAAS) in an air-acetylene flame, according to the user's manual, provided by the manufacturer. Lead and cadmium hollow cathode lamps were used as the radiation source with wavelength of 283.3 and 228.8 nm, respectively. A digital pH meter, WTW Metrohm 827 Ion analyzer (Herisau, Switzerland), equipped with a combined glass calomel electrode was used for the pH adjustments at 25±1 °C temperature. Heidolph heater stirrer model MR 3001 (Germany) was employed for heating and stirring of the solutions. Fourier transform infrared (FT-IR) spectra (4,000–200 cm⁻¹) in KBr were recorded using Bruker IFS66/S FT-IR spectrometer. 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. 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.

Material and Reagents

Sodium nitrite, 4-nitrobenzaldehyde, 1-(2-pyridylazo)-2-naphthol (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 μ m and surface area of 200 m²/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. Stock standard solutions (100 mg/L) of corresponding analytes were prepared with the addition of an appropriate amount of nitrate salts in ultra-pure water while working standard of metals were prepared from the dilution of stock standard solution with distilled water. Soil (NCS DC 73323) and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326) from Bulgaria were prepared as the reference materials.

Preparation of 1-(2-Pyridylazo)-2-Naphthol-Functionalized Organic–Inorganic Hybrid Mesoporous Materials

MCM-48 mesoporous 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-amino-propyltriethoxysilane (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 1-(2-pyridylazo)-2-naphthol-functionalized mesoporous silica (PAN-MCM-48) was confirmed by IR spectroscopy, low-angle X-ray diffraction, elemental and thermal analysis, and N_2 adsorption surface area measurement.

Extraction Procedure

The optimized values by this optimization method were 10 mg, 8 min, 6.3, HCl, 1.6 mL, 1.2 mol L⁻¹ HCl, and 10 min, for amount of sorbent, retention time, pH of solution, type, volume, concentration of the eluent, and elution time, respectively. Batch experiments were used for investigation of factors in sorption and desorption steps. Simultaneous extraction of cadmium and lead ions from the solution is followed by two steps: sorption and desorption. In the sorption step, the pH of the sample solution was adjusted to 6.3 by drop wise addition of 2 mol L⁻¹ sodium hydroxide or nitric acid solutions. Then, 10 mg of dried sorbent was suspended in aqueous solution containing 1 mg L⁻¹ of cadmium and lead ions and stirred for 8 min with a magnetic stirrer. In the desorption step,

simultaneous elution of lead and cadmium ions from the sorbent was performed by 1.6 mL of HCl (1.2 mol L⁻¹). After 10 min, the concentration of cadmium and lead ions in this solution was determined by flame atomic absorption spectrometry (FAAS).

Real Sample Pretreatment

The tested water samples were distilled, tap (Tehran, Iran), and sea water (Persian Gulf and Caspian Sea). The water samples were collected in polyethylene bottles. They were cleaned with acid bath, and then filtered through nylon filters (Millipore, 0.22 μ m) before the analysis. Soil samples were collected from Mouteh gold mine (Iran). A 0.2-g of homogenized soil sample and certified reference materials (CRM) was accurately weighed in a 100-mL beaker. The sample was digested by using a mixture of HNO₃–HCl (aqua regia) on a hot plate at 100 °C for 1 h, till the clear transparent solutions were obtained. After cooling, the resulting solutions were filtered through a 0.45- μ m pore size membrane filter into a 100-mL conical bottom flask and were diluted with distilled water (diluted to 75 mL). Afterwards, pH of soil samples was adjusted to desired pH and then was subjected to developed procedure as described in Section 2.4 and subsequent determination of cadmium and lead ions by FAAS. Blanks were also treated in the same manner as samples were treated but without analyte.

The shrimps and fishes were bought from four local supermarkets in four different sites randomly near the Persian Gulf, Iran. After collection, four samples of seafood (fish and shrimp) from each supermarket were randomly selected, mixed, and transferred into an ice bag and transported to the laboratory and stored at –20 °C prior to analysis. The sampling was carried out on August 2012. The muscle tissues of the shrimps and fishes were separated and freeze-dried in order to obtain a constant weight, and were finely grounded. For metal analysis, approximately 1.0 g of the grounded samples was digested in 5 mL of concentrated nitric acid at 135 °C for 4 h, and then, 1 mL of hydrogen peroxide (30 %) and 1 ml of concentrated perchloric acid were added, and the temperature maintained at 150 °C until the liquid was clear (Zhou et al. 1998; Wua and Yang 2011). Then, the resulted solution was filtered and after the filtration, the clear solution was diluted to 75 mL and the pH was adjusted to 6.3 using NaOH or HNO₃ for further analysis.

Results and Discussion

Characterization of 1-(2-Pyridylazo)-2-Naphthol-Functionalized Organic–Inorganic Hybrid Mesoporous Materials

The MCM-48 mesoporous 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 a surface area of $1,026 \text{ m}^2 \text{ g}^{-1}$ for the mesoporous silica which indicates that the material has a mesopore structure. After functionalization of the MCM-48 with 3-amino-propyltriethoxysilane agent [34], 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 were carried out according to previous report (Liu et al. 1995). Formation of PAN-MCM-48 mesoporous 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 $1,608 \text{ cm}^{-1}$ ($N=N$), $1,598 \text{ cm}^{-1}$ (C-C aromatic ring), $1,281 \text{ cm}^{-1}$ (C-N), $2,983 \text{ cm}^{-1}$ (aliphatic C-H), and $3,027 \text{ cm}^{-1}$ (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 $1,026$ to $574 \text{ m}^2 \text{ g}^{-1}$ after functionalization, PAN is mainly grafted within the channels of mesoporous 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 un-functionalized MCM-48 (Fig. 2). According to this pattern, the mesopore structure of MCM-48 remains intact after functionalization. For further investigation of the mesoporous structure of the sorbent which is a key point in its efficiency, the TEM study was carried out and the result also confirmed that the mesoporous structure of the MCM-48 (Fig. 3a) has been retained after functionalization (Fig. 3b). The pores (bright spots) and walls (dark spots) are clearly visible from TEM micrographs in Fig. 3. The thermal stability of PAN-MCM-48 has been investigated by TGA/DSC analysis. According to the TGA/DSC analysis, the sorbent is stable up to $160 \text{ }^\circ\text{C}$. Moreover, about 37 % of loss weigh is in good

agreement with the elemental analysis results about PAN concentration grafted on mesoporous silica (Fig. 4).

Optimization Experiments

The affecting parameters on adsorption and desorption steps were optimized by a Box-Behnken design through response surface methodology. Three variables (pH value, extraction time, and amount of the synthesized sorbent) were selected as the main factors affecting the sorption step, while four variables (type of eluent, volume of the eluent, concentration of the eluent, and elution time) were selected for the desorption step in the optimization study.

Optimization of Retention Parameters

The Box-Behnken design (BBD) is an efficient option (three-level factor quadratic design) in which the experimental points are located on the midpoints of the edges of a cube and at the center (central points). The levels of factors selected based on primary experiments based on one variable at the time are shown in Table 1. In a system involving three independent variables $\times 1$, $\times 2$, and $\times 3$ the responses of the Box-Behnken design can be expressed by the following quadratic polynomial equation:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 \times 2 + \beta_{13} x_1 \times 3 + \beta_{23} x_2 \times 3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 \quad (1)$$

where y is the response, β_0 is a constant and β_1 – β_{33} are the regression coefficients. The number of experimental points (N) can be defined by the following expression:

$$N = 2K(K-1) + C0 \quad (2)$$

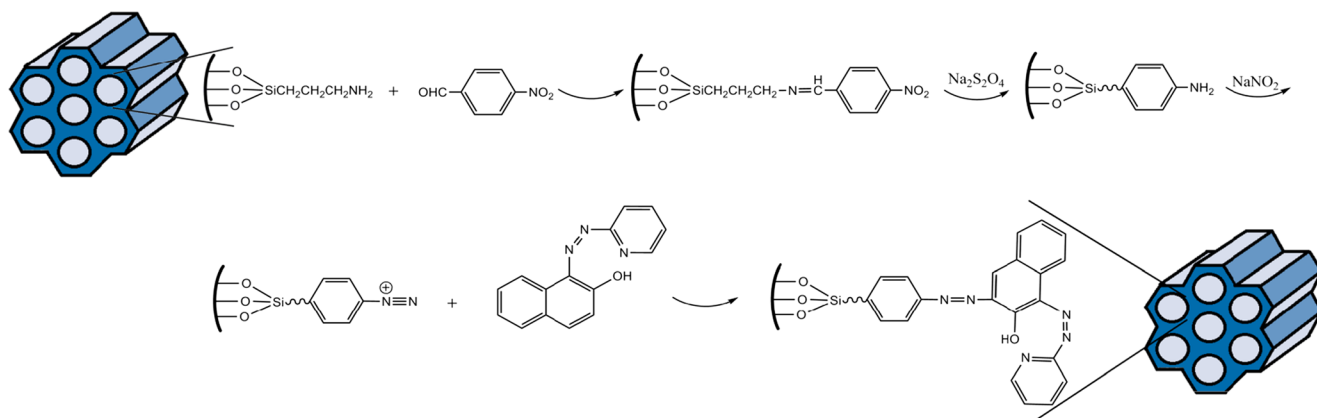
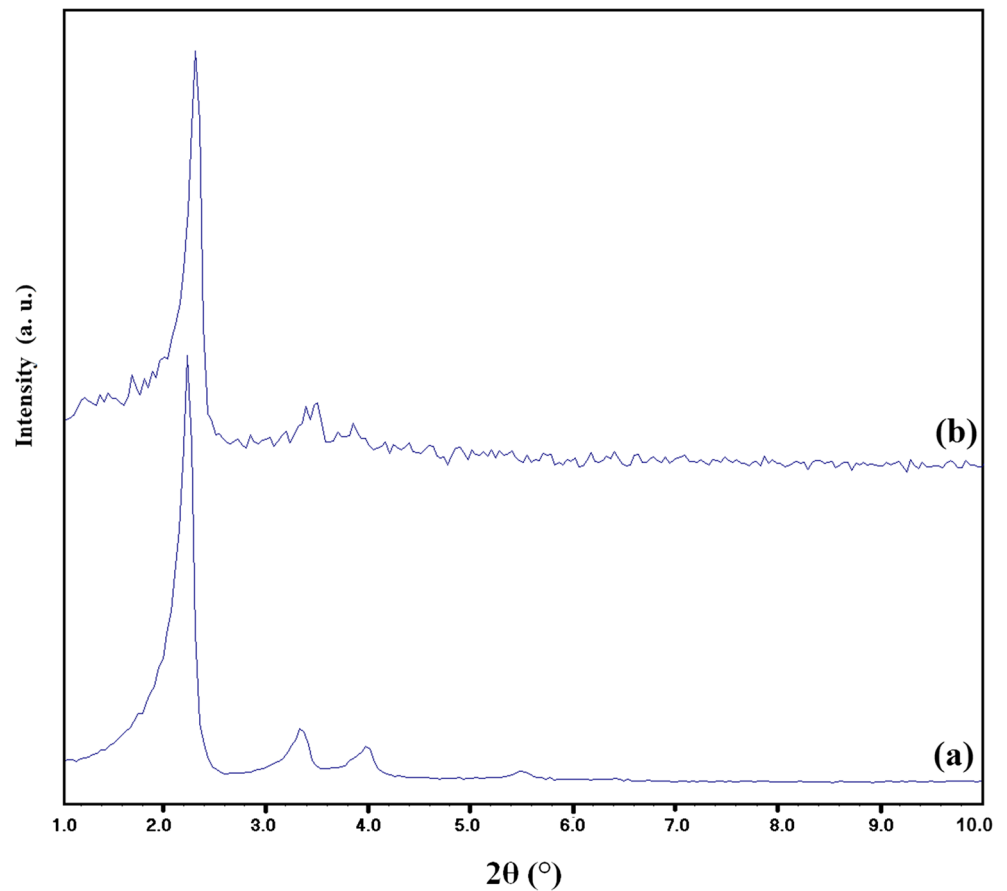


Fig. 1 A scheme to illustrate preparation of modifying 1-(2-Pyridylazo)-2-naphthol-functionalized organic-inorganic hybrid porous materials

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



where K is the number of parameters and $C0$ is the number of center points. In this step, K and $C0$ were set at 3 and

therefore 15 experiments had to be done. The effects of variables on the retention step by using the Pareto chart are

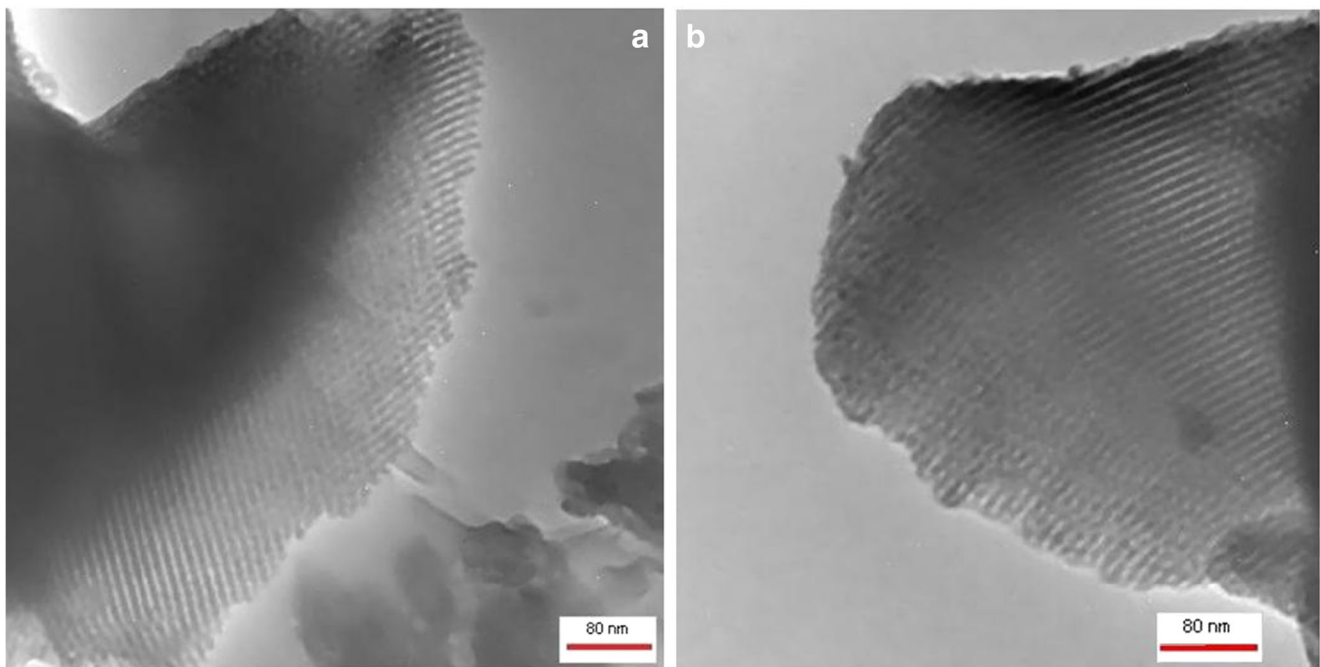
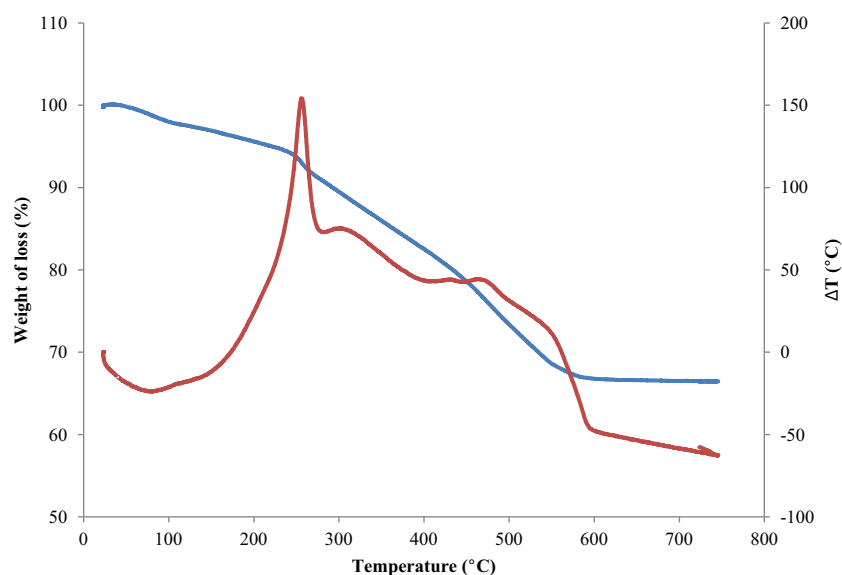


Fig. 3 TEM micrograph of MCM-48 (a) and 1-(2-pyridylazo)-2-naphthol modified MCM-48 (b)

Fig. 4 TGA/DSC analysis of 1-(2-Pyridylazo)-2-naphthol-functionalized organic–inorganic hybrid porous



shown in Fig. 5a. The bars, extending beyond the line, correspond to effects that are statistically significant at the 95 % confidence level. Enhancement or reduction of the response are shown with the positive or negative sign (corresponding to a colorless or colored), respectively. The results expressed that the pH of solution has the main effect on the retention step. The best pH for simultaneous sorption of analyte was found to be 6.3. This observation could be attributed to the fact that in high pH, the analyte ions precipitate as their hydroxide salts which cause reducing of the retention. Moreover, in low pH, the active groups of 1-(2-Pyridylazo)-2-naphthol will be protonated and could not coordinate to lead and cadmium ions. A sorption time of about 8 min was required for quantitative retention of the analytes from solution into solid phase. Furthermore, the amount of PAN-MCM-48 has a negative insignificant effect on the extraction process. Due to the high viscosity of the solution, the retention of cadmium and lead ions decreased in higher amounts of the sorbent. The response surface methodology (RSM) in Fig. 5b represents simultaneous effects of two variables (amount of sorbent and sorption time) on the retention of cadmium and lead ions. According to the overall results of the optimization study, pH=6.3, sorption

time=8 min, and amount of sorbent=10 mg were chosen for the sorption step.

Selection of Elution Solvent Type

Complete removal of lead and cadmium ions from synthesized sorbent is a very crucial step to guarantee the absence of memory effect. For investigation of eluent's type, elution of metal ions from the sorbent was studied using 2 mL of three solvents such as HCl, HNO₃, and CH₃COOH. Based on the results in Table 2, HCl showed a better recovery compared to other solvents. Therefore, HCl was selected as the eluent for further studies.

Optimization of Desorption Step

In this step, the Box-Behnken design was employed for desorption step while other factors were optimized in the previous section. Eluent concentration (mol L⁻¹), eluent volume (mL), and elution time (min) were investigated in the elution step using the Box-Behnken design. According to BBD, eluent concentration and volume showed positive and

Table 1 Experimental variables and levels of the Box-Behnken design (BBD)

	Variable	Levels		
		Lower	Central	Higher
Retention parameters	A: pH	2	5.5	9
	B: Amount of the sorbent (mg)	10	20	30
	C: Sorption time (min)	5	10	15
Desorption parameters	A: Eluent concentration (mol L ⁻¹)	0.5	1	1.5
	B: Eluent volume (mL)	0.75	1.4	2
	C: Elution time (min)	5	10	15

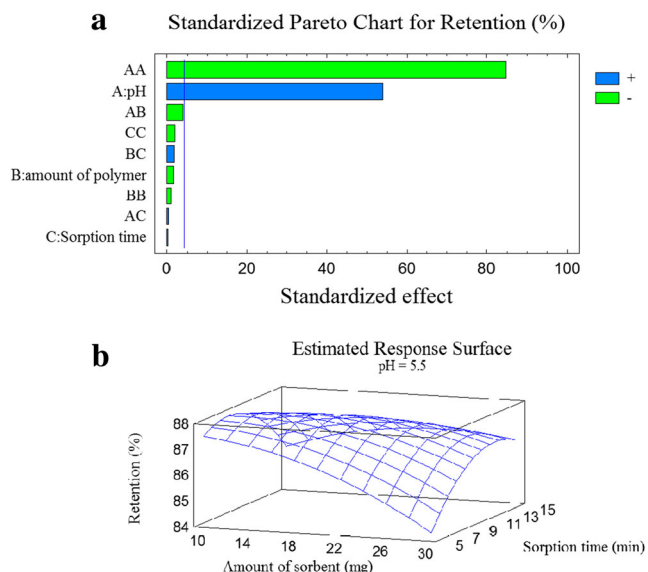


Fig. 5 a Pareto chart of the main effects in the BBD. AA, BB, and CC are the quadratic effects of the pH, amount of the sorbent and sorption time, respectively. AB, AC, and BC are the interaction effects between pH and amount of the sorbent, pH and sorption time, and amount of the sorbent and sorption time, respectively. b The estimated response surface of amount of the sorbent and sorption time

significant effect on the recovery of target ions but elution time showed a negative and non-significant effect [Pareto chart (Fig. 6a)]. Simultaneous effects of eluent concentration and eluent volume on the response were investigated with the aid of RSM (Fig. 6b). According to the overall results, eluent concentration=1.2 mol L⁻¹, elution volume=1.6 mL, and elution time=10 min were chosen for desorption of target ions from the synthesized sorbent.

Effect of Sample Volume

In the analysis of real samples, the sample volume is one of the important parameters influencing the preconcentration factor. Therefore, the effect of sample volume on simultaneous quantitative retention of cadmium and lead ions by the synthesized

Table 2 Effect of type of eluent on recovery of cadmium and lead ions from the synthesized sorbent (Conditions: sample pH 6.3, sorption time 8 min, elution time 10 min)

Eluent	Concentration (mol L ⁻¹)	Volume (mL)	Recovery (%±Sd) ^a	
			Lead	Cadmium
HCl	1.5	2	99.0±1.0	99.0±1.0
HCl:HNO ₃	1:1	2	96.0±1.0	98.0±1.0
HNO ₃	1.5	2	88.0±1.0	90.0±2.0
HCl: CH ₃ COOH	1:1	2	90.0±1.0	93.0±1.0
HNO ₃ : CH ₃ COOH	1:1	2	81.0±1.0	84.0±1.0
CH ₃ COOH	1.5	2	47.0±2.0	38.0±2.0

^a Standard deviation (N=3)

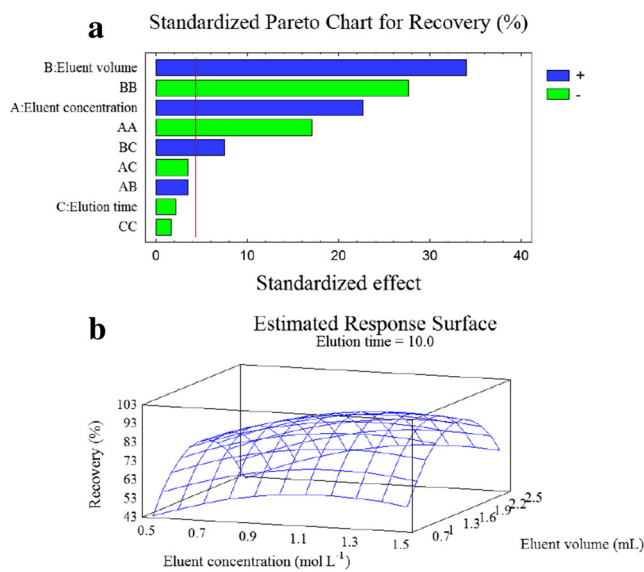


Fig. 6 a Pareto chart of the main effects in the BBD. AA, BB, and CC are the quadratic effects of the eluent concentration, eluent volume, and elution time, respectively. AB, AC, and BC are the interaction effects between eluent concentration and eluent volume, eluent concentration and elution time, and eluent volume and elution time, respectively. b The estimated response surface of eluent concentration and eluent volume

sorbent was investigated. For this purpose, 10 mg of the sorbent was suspended in different sample volumes (25, 50, 100, 200, 300, 350, 400, 425, 450, 475, and 500 mL) containing 16 µg of cadmium and lead ions. All solutions were extracted under optimum condition by the method and then eluted under optimized desorption parameters. It was found that the simultaneous quantitative recovery (Fig. 7) of cadmium (300 mL) and lead (450 mL) ions on PAN-MCM-48 could be obtained for sample volume up to 300 mL.

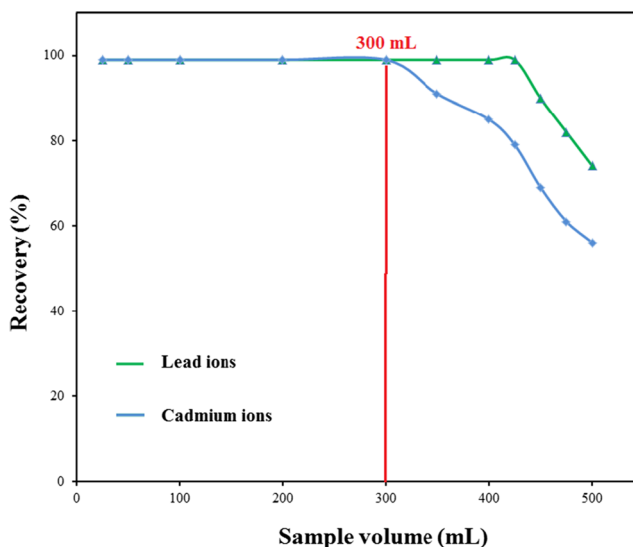


Fig. 7 The effect of sample volume on the recovery of cadmium and lead ions on the 1-(2-Pyridylazo)-2-naphthol-functionalized organic-inorganic hybrid porous materials (Conditions: sample pH 6.3, 16 µg of cadmium and lead ions, sorption time 8 min, eluent 1.6 mL of HCl (1.2 mol L⁻¹), elution time 10 min)

Table 3 The tolerance limit of various ions on the determination of cadmium and lead ions (Conditions: sample pH 6.3, sample volume 50 mL, 0.5 µg of cadmium and lead ions, sorption time 8 min, eluent 1.6 mL of HCl (1.2 mol L⁻¹), elution time 10 min)

Interfering ion	Tolerable concentration ratio X/Cd and Pb ions	R ^a (%±S) ^b	
		Cd ²⁺	Pb ²⁺
K ⁺	10,000	99.0±1.0	99.0±1.0
Ag ⁺	10,000	99.0±1.0	99.0±1.0
Na ⁺	10,000	98.0±1.1	99.0±1.0
Cs ⁺	10,000	98.0±1.2	98.0±1.5
Ca ²⁺	900	97.2±0.9	97.8±1.1
Mg ²⁺	800	97.1±1.1	97.6±1.4
Al ³⁺	800	97.9±1.2	97.4±1.2
Fe ²⁺	700	97.2±1.2	97.5±1.3
Ni ²⁺	700	97.9±0.8	98.1±0.6
Mn ²⁺	600	97.4±0.6	98.3±0.7
Cu ²⁺	600	96.4±1.2	97.4±1.2
Cr ³⁺	600	97.3±1.1	97.6±0.9

X concentration of diverse ions

^a Recovery

^b Standard deviation

Sorption Capacity of the 1-(2-Pyridylazo)-2-Naphthol-Functionalized Organic–Inorganic Hybrid Mesoporous Materials

The sorption capacity defined as the maximum amount of metal ions sorbed per gram of the sorbent is an important factor for evaluation of the synthesized mesoporous material. To evaluate this factor, 100 ml of a solution containing 30 mg cadmium and lead ions was applied to the extraction method and the sorption capacity was calculated at the optimized extraction conditions. In order to evaluate the maximum adsorption capacity, the difference between concentration of the solution before extraction and the concentration of the solution after extraction was calculated. The sorption capacities of the sorbent were calculated to be 210 and 254 mg g⁻¹ for cadmium and lead ions, respectively. Obviously, the adsorption capacity of the synthesized mesoporous sorbent was larger than previous synthesized sorbent.

Table 4 Statistical and calibration parameters for lead and cadmium detection by the proposed method

Analyte	LOD (µg L ⁻¹)	LOQ (µg L ⁻¹)	DLR (µg L ⁻¹)	Regression equation	r ²	PF	Relative recovery ^a (%)
Lead	0.9	2	2–500	Y=1.819 C ^b +0.0005	0.99	127.2	98.2
Cadmium	0.04	0.1	0.1–40	Y=29.403 C ^b +0.0015	0.99	367.5	98.8

^a Relative recovery was found for 10 µg L⁻¹ of lead and cadmium ions

^b Concentration of lead and cadmium ions (mg L⁻¹)

Table 5 Determination of cadmium and lead ions in certified reference materials by the proposed solid phase extraction method

Sample	Element	Concentration (mg Kg ⁻¹)		Relative error (%)
		Certified value	Founded	
Ore polymetallic gold Zidarovo-PMZrZ (206 BG 326)	Lead	5.47	5.38	-1.6
Soil (NCS DC 73323)	Cadmium	0.45	0.44	-2.2

The Effect of the Potentially 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 50 mL of solution containing 0.5 µg of cadmium and 0.5 µg of lead ions. The degree of tolerance for some alkaline, alkaline earth, and transition metal ions are presented in Table 3. From the tolerance data, it can be seen that the potentially interfering ions have no significant effects on preconcentration of cadmium and lead ions at pH of 6.3.

Reusability of the Solid Material

The long-term stability of the sorbent as solid phase was investigated by successive sorption and elution cycles of solutions of 100 µg L⁻¹ Pb and Cd ions at the optimum condition. Afterwards, the adsorbed metal ions were eluted with 1.2 mL of 1.6 mol L⁻¹ HCl solution. By monitoring the change in the recoveries of the extraction of Pb and Cd, the stability of the sorbent was estimated. The results show that the sorbent is stable after eight and ten adsorption–desorption cycles for cadmium and lead ions, respectively.

Statistical and Calibration Parameters

The performance of PAN-functionalized organic–inorganic hybrid mesoporous materials was investigated at the optimum conditions. The limit of detection (LOD), regression equations, coefficient of determination (R²), linear dynamic ranges (LDRs), preconcentration factors (PFs), and relative recoveries (RR %) were obtained. The limits of detection, defined as

$C_{LOD}=3S_b/m$, where S_b is the standard deviation of seven replicate blank signals and m is the slope of the linear section of calibration curve after preconcentration for a sample volume of 75 mL. Precision was expressed as a mean percentage of the relative standard deviation (RSD %). Also, the

preconcentration factor calculated as the ratio between the slopes of the calibration curves acquired by the proposed method ($Y=1.819 X+0.0005$ for lead ions and $Y=29.403 X+0.0015$ for cadmium ions) and through the direct analysis of cadmium and lead ions by FAAS ($Y=0.0143 X+0.0063$ for

Table 6 Analysis of lead and cadmium ions in different water and soil samples (The number of replicate=3)

Sample	Ion	Added ($\mu\text{g L}^{-1}$)	Founded ($\mu\text{g L}^{-1}$)	RR (%)	RSD (%)
Distilled water	Cadmium	–	–	–	–
		5.0	4.9	98.0	2.2
		30.0	29.8	99.3	2.8
	Lead	–	–	–	–
		5.0	4.9	98.0	2.5
		30.0	29.7	99.0	2.6
Tap water	Cadmium	–	–	–	–
		5.0	4.9	98.0	2.4
		30.0	29.6	98.6	2.9
	Lead	–	–	–	–
		5.0	4.9	98.8	2.3
		30.0	29.8	99.3	2.5
Caspian Sea water	Cadmium	–	2.1	–	2.7
		5.0	6.9	96.0	3.1
		30.0	31.9	99.3	2.8
	Lead	–	11.9	–	2.9
		5.00	16.8	98.0	2.7
		30.00	41.5	98.6	3.2
Persian Gulf water	Cadmium	–	4.1	–	2.9
		5.0	9.2	102.0	3.1
		30.0	33.8	99.0	3.2
	Lead	–	18.2	–	3.1
		5.00	23.1	98.0	3.1
		30.00	47.9	99.0	3.4
Sample	Ion	Added ($\mu\text{g}\cdot\text{Kg}^{-1}$)	Founded ($\mu\text{g}\cdot\text{Kg}^{-1}$)	RR (%)	RSD (%)
Mouteh gold mine soil	Cadmium	–	5.1	–	2.9
		5.0	9.9	96.0	3.2
		30.0	34.9	99.3	3.4
	Lead	–	10.2	–	2.7
		5.0	15.1	98.0	3.1
		30.0	39.8	98.6	2.9
Fish sample	Cadmium	–	8.9	–	2.7
		5.0	13.8	98.0	3.1
		30.0	38.7	99.3	3.3
	Lead	–	42.2	–	3.2
		5.0	47.1	98.0	3.4
		30.0	71.9	99.0	3.2
Shrimp sample	Cadmium	–	7.2	–	2.9
		5.0	12.1	98.0	3.1
		30.0	36.9	99.0	3.4
	Lead	–	45.2	–	3.1
		5.0	50.0	96.0	3.3
		30.0	74.9	99.0	3.3

Table 7 A comparison between the proposed solid phase extraction based on PAN-functionalized organic–inorganic hybrid mesoporous materials with previous works

Method	LOD ($\mu\text{g L}^{-1}$)		RSD (%)		SC ^a (mg g^{-1})		PF		Ref.
	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	
Solid sulfur-FAAS	0.2	3.2	4.7	5.1	0.0034	0.0156	250	250	Parham et al. 2009
MOF-FAAS	–	0.5	–	<4 %	–	120	–	100	Nabid et al. 2012
MWCNTs/P2AT-FAAS	0.3	1	2.4	3.2	178	186	100	100	Salarian et al. 2014
DPC-SBA-15	0.15	–	3.4	–	198	–	100	–	Bagheri et al. 2012a
DTZ-NPF	0.025	1.0	3.4	2.4	101	186.4	480	280	Behbahani et al. 2013a
DTZ-SBA-15	0.09	0.45	3.8	3.1	189	208	100	100	Behbahani et al. 2013b
PAN-MCM-48-FAAS	0.04	0.9	2.1	2.8	210	254	367.5	127.2	This work

^a Sorption capacity

lead ions and $Y=0.08X+0.001$) was found to be 127.2 (1.819/0.0143=127.2) and 367.5 (29.403/0.08=367.5) for lead and cadmium ions, respectively. The analytical performances of the proposed method were summarized in Table 4.

Certified Reference Material Analysis

Soil (NCS DC 73323) and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326) with a certified cadmium and lead content were applied as certified reference material. As Table 5 shows, a good correlation was obtained between the certified amounts and the amounts found by the method. Therefore, PAN-functionalized organic–inorganic hybrid mesoporous materials can be used as a reliable solid phase technique for separation and trace determination of cadmium and lead ions in environmental samples.

Real Sample Analysis

To evaluate the capability of this solid phase extraction technique for trace analysis of lead and cadmium ions in real samples with different matrices containing various amounts of diverse ions, the method was used for the extraction of cadmium and lead ions from different samples (Table 6). The relative recoveries percentage of lead and cadmium ions from the real and spiked samples varied in the range of 96.0–102 %. The results clearly indicate the suitability of the PAN-functionalized organic–inorganic hybrid mesoporous materials for the preconcentration and determination of cadmium and lead ions at trace levels in environmental samples.

Comparison of the Synthesized PAN-Functionalized Organic–Inorganic Hybrid Mesoporous Materials with Literature

The proposed method was compared with other reported methods in literatures. According to Table 7, the introduced

solid phase extraction method is clearly better than other reports in LOD, sorption capacity, PF, RSD, and extraction time (Parham et al. 2009; Salarian et al. 2014; Nabid et al. 2012; Bagheri et al. 2012a; Behbahani et al. 2013a; Behbahani et al. 2013b).

Conclusion

In the present study, an application of 1-(2-Pyridylazo)-2-naphthol-functionalized organic–inorganic hybrid mesoporous material was introduced in the area of solid phase extraction. The mesoporous structure of PAN-MCM-48 can cause the fast adsorption of lead and cadmium ions. The affecting parameters on adsorption and desorption steps were optimized by the Box-Behnken design through response surface methodology. Determination of the lead and cadmium ions resulted in good quantitative recoveries in food, water, and soil samples. 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 better than other solid phase extraction methods.

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Compliance with Ethics Requirements

Conflict of Interest Hamid Reza Fouladian declares that he has no conflict of interest. Mohammad Behbahani declares that he has no conflict of interest. This article does not contain any studies with human or animal subjects.

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