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Extraction of Nickel from Soil, Water, Fish, and Plants on Novel Pyridine-Functionalized MCM-41 and MCM-48 Nanoporous Silicas and Its Subsequent Determination by FAAS

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Abstract Nickel is considered as an important toxic pollutant and is continuously released into the biosphere by some anthropogenic activities such as industrial and urban sewage. The main objective of this study was to determine the concentration of nickel in different samples of soil, water, and muscle tissue of fish species which were collected from the Persian Gulf. For this propose, a simple and sensitive solid-phase extraction using pyridine-functionalized Mobil Composition of Matter (MCM)-41 and MCM-48 nanoporous silica was developed and their application in preconcentration and determination of nickel by flame atomic absorption spectrometry was studied. Limit of detection was found to be lower than 3.5 μg L^{-1}. Recovery and precision of the method were above 98.5% and below 1.5%, respectively. To gauge their ability in terms of application to natural samples, the proposed method was applied to a number of natural samples including plants, water, soil and fish species, and the amount of nickel was determined by spiking known concentrations of nickel into the solution. The results show that pollution of soil and water has some effects on bioaccumulation of Ni on marine organisms and plants that could magnify along the food chain.

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Keywords Solid phase extraction · Pyridine-functionalized nanoporous silica · MCM-41 · MCM-48 · Nickel

Introduction

Branded as a potential carcinogenic agent and listed in group 2B by the International Agency for Research on Cancer, nickel is garnering a lot of attention due to its pathogenic properties (Yano et al. 1998). Human may be exposed to nickel by drinking water and breathing. It enters aquatic systems through anthropogenic activities such as mining, fuel combustion, waste incineration, etc. or through discharge of effluents containing nickel. The elevated level of nickel in the environment is a cause for concern. Excluding the higher chances of development of lung and prostate cancer (Kalyakina et al. 2003; Kasprzak et al. 2003), uptake of exceedingly large quantities gives rise to heart disorders, birth defects, and a variety of respiratory system failures. Hence, its determination in trace amounts in the environment is important (Karve and Rajgor 2009).

The instrument most frequently utilized for the determination of nickel is considered to be flame atomic absorption spectrometry (FAAS). However, this method has its own drawbacks and notably is encumbered by low sensitivity and detection limit as well as sample matrix implications. Evidently, separation and preconcentration are a prerequisite for accurate and sensitive detection of the trace amounts of nickel in the presence of matrix elements (Karve and Rajgor 2009). Although, the graphite furnace atomic absorption spectrometry is a powerful analytical tool for determining the trace elements in environmental samples, preconcentration and separation techniques are still unavoidable (Sun et al. 2006). Liquid–liquid extraction (Popova et al. 1991), coprecipitation (Chen et al. 1997), ion exchange (Wang and Hansen 2000), and solid-phase extraction (SPE) are the most common techniques for separation and preconcentration of nickel (Gopikrishna et al. 2004; Taher 1999; Yunes et al. 2003; Suvardhan et al. 2004). Among the aforementioned methods, SPE has widely been utilized for the preconcentration and separation of metals due to a number of advantages, namely higher enrichment factors, the absence of emulsion, safety with respect to hazardous samples, minimal costs as a result of low consumption of reagents, flexibility, and ease of automation (Pyrzynska and Trojanowicz 1999; Liu et al. 2004; Soylak et al. 2003; Soylak et al. 1997; Poole 2003). SPE methods for separation of trace amounts of nickel using C_{18} cartridges (Khorrami et al. 2006; Khorrami et al. 2004), silica gel (Xie et al. 2008; Sarkar et al. 2002; Alan et al. 2007), Amberlite series resins (Tewari and Singh 2001), Merrifield's chloromethylated styrene divinylbenzene resins (Seyhan et al. 2007), Ambersorb and chromosorb resins (Baytak and Turker 2006), activated carbon (Mikuła and Puzio 2007), cellulose (Gurnani et al. 2003), and polyurethane foam (Moawed and El-Shahat 2006) has been developed. In spite of a considerable amount of work carried out in the field of solid-phase extraction in the last decade, the search for better adsorbents continues to thrive. In this context, nanoporous silica materials have drawn extensive attention (Kresge et al. 1992; Beck et al. 1992) and already applied to fields ranging from catalysis (Iwanami et al. 2009) and nanotechnology (He et al. 2006) to biotechnology (Stead et al. 2009).

Nanoporous silica first synthesized by Mobil's researchers in 1992, Mobil Composition of Matter (MCM) is the initial name given to a series of nanoporous materials. MCM-41 and MCM-48 are two of the most popular nanoporous molecular sieves eagerly studied by researchers. Despite being composed of amorphous silica wall, the most arresting fact about them is that they exhibit long range ordered framework with uniform nanoporous. In addition, the pore diameter of these materials can easily be controlled within nanoporous range (1.5–20 nm) by adjusting the synthesis conditions and/or by employing surfactants with different chain lengths in their preparation. MCM-41 and MCM-48 nanoporous silicas with large and uniform pore size, large surface area, thermal stability, and mild acidic property have proven to be suitable to be used as an adsorbent according to prior studies (Morin et al. 1997; Kumar et al. 2002). In order to improve their ability to absorb metals, it is essential to functionalize MCMs with certain groups. Younesi et al. (Heidari et al. 2009) investigated the application of functionalized MCM-41 for the removal of Ni(II), Cd(II) and Pb(II) ions from aqueous solutions. Aside from the aforementioned case, up to now, most researches have been focused on the hexagonal-phase nanoporous silica, MCM-41, with a uniform one-dimensional pore network. Hardly has any study been devoted to MCM-48 with the three-dimensional and cubic pore system.

In this work and for the first time, the application of pyridine-functionalized MCM-41 (py-MCM-41) and MCM-48 (py-MCM-48) silica as a solid-phase for separation of nickel from aqueous solutions was investigated. The effects of eluent type, eluent concentration, solution pH, flow rate, metal ion concentrations, and adsorption capacity and efficiency of py-MCM-41 and py-MCM-48 were studied. The proposed method was applied to a number of industrial and natural samples and its accuracy and precision was measured using several standard materials.

Experimental

Material and Methods

All of the reagents were of analytical grade and used without further purification. Standard solution of nickel with concentration of 1,000 μg mL^{-1} was purchased from Merck (Darmstadt, Germany). Working solutions of Ni were prepared by diluting appropriate amounts of the stock solutions with buffer solutions. Buffer solutions were utilized to adjust the pH of the solutions. For the pH 1 and 4, trisodium citrate/hydrochloric acid buffer solutions were used. Acetic acid/sodium acetate buffers were used to adjust pH in the range of 4–6, while sodium hydrogen phosphate/disodium hydrogen phosphate buffers were used for pH 6–10. A Milli-Q (Millipore, Bedford, MA, USA) purification system was employed to provide the deionized water needed to prepare all the required solutions. HCl and HNO_3 were purchased from Merck (Darmstadt, Germany).

Apparatus

An AA-680 Shimadzu (Kyoto, Japan) FAAS in an air–acetylene flame was used to determine the concentration of Ni(II) ions. A nickel hollow cathode lamp was used as the radiation source with wavelength set at 232.0 nm. All pH measurements were made at 25±1 °C with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass–calomel electrode. Analysis regarding flow rate were performed using a vacuum pump obtained from Leybold (Germany). An adjustable vacuumed gauge and controller were obtained from

Analytichem International (Harber City, CA, USA). The CHN analyses were performed on a Thermo Finnigan Flash-1112EA microanalyzer (Italy). A Milestone Ethos D closed vessel microwave system (maximum pressure 1,450 psi, maximum temperature 300 °C) was used.

Procedure

Preparation of Functionalized Nanoporous Silica

N-[3-(triethoxysilyl)propyl]isonicotinamide (TPI; Hoogbomm et al. 2005), MCM-41-Si (Schumacher et al. 1999), and MCM-48-Si (Nunes et al. 2002) were prepared according to previous reports. Both nanoporous silicas were functionalized with TPI, similar to the percedure used for functionalization of nanoporous silica with amine (Jhonson and Stein 2001). In a typical reaction, 1.0 g of MCM-41 or MCM-48 was suspended in 50 mL of toluene and the mixture was stirred for 1 h. Subsequently, 2.0 g of TPI was added and the mixture was refluxed for 2 h. The white–brownish solid was removed from the solvent by filtration and was washed with toluene and chloroform and dried at room temperature (Fig. 1). IR (KBr, per centimeter): Py-MCM-41 and py-MCM-48: 3445 (NH), 3045 (CH, aromatic) 2927 (CH, aliphatic) 1653 (CO), 1551 (C=C), 1080 (Si-O-Si). Elemental analysis of py-MCM-41, py-MCM-48 samples gave pyridine concentrations of 1.80 and 1.83 mmol g^{-1}, respectively.

Sample Collection and Preparation

Tap water (Tehran, Iran), river water (Babolrud River, Babol, Iran), and Persian Gulf water (Bandar Imam, Khuzestan, Iran) were used as water samples. They were collected in cleaned polyethylene bottles and were filtered through a 0.45 μm pore size nylon filter (Millipore) right away after sampling. In addition, vegetable samples, "*Zataria multiflora*" Boiss, "*Apocynaceae*", and "*Citrullus colocynthis*" were collected around the Persian Gulf Petrochemical Company with the distance of almost 20 km. A layer of soil with the depth of 5 cm was collected in each sampling process with the distance of 10, 15, 20, 25, and 30 km. Fish samples, *Flounder fish*, *Lion fish*, and "*Stromateus cinereus*" were collected in Persian Gulf. All samples were collected over a period of 12 weeks during the spring of the year of 2011 and each time five samples were gathered.

A soil (NCS DC 73323) from the China National Analysis Center for Iron and Steel was used as standard material samples with certified nickel content. Reference materials and soil samples were digested with 6 mL of HCl (37%) and 2 mL of HNO_3 (65%) in a microwave digestion system. 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. The residue from digestion was then diluted with deionized water, as well as a blank digestion (ACS Committee on Environment Improvement 1980).

The muscle tissues of fish samples were digested with concentrated HNO_3 and then were transferred into 100-mL Teflon beakers and 10 mL nitric acid was added. Afterward, the sample was heated at 280 °C on a hot plate for 2 h. Then 2 mL of HNO_3 1 mol L^{-1} was added to the residue and the solution was evaporated again and continued until complete digestion. After cooling, 10 mL of HNO_3 1 mol L^{-1} was added and diluted and filtered through a membrane filter (with 0.45 μm pores). One standard material DORM-2 (National Research Council Canada, Ottawa, Ontario, Canada) with the certified amount of Ni was analyzed to determine the concentration of Ni ions in *Dogfish* muscle.

After washing vegetables with distilled water, 10.0 g of each of the grounded samples was dried at 80 °C and

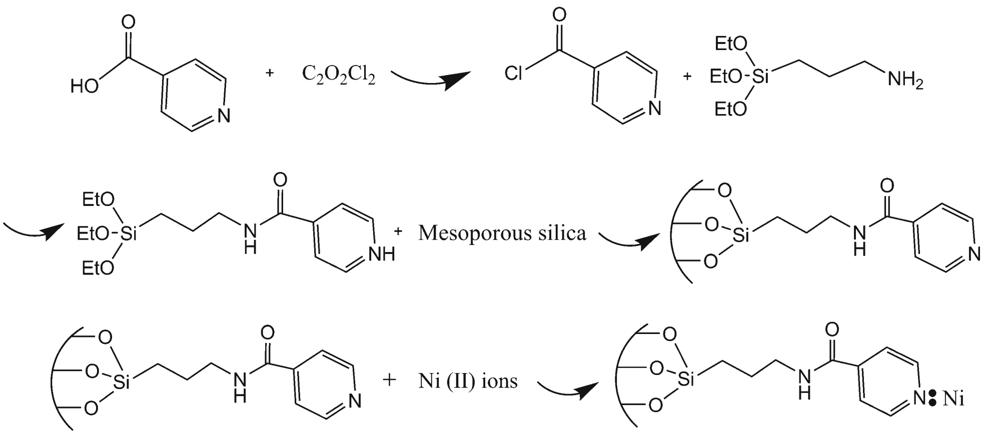

Fig. 1 A schematic model for modifying nanoporous (MCM-41, MCM-48) with pyridine, and adsorption of Ni(II)

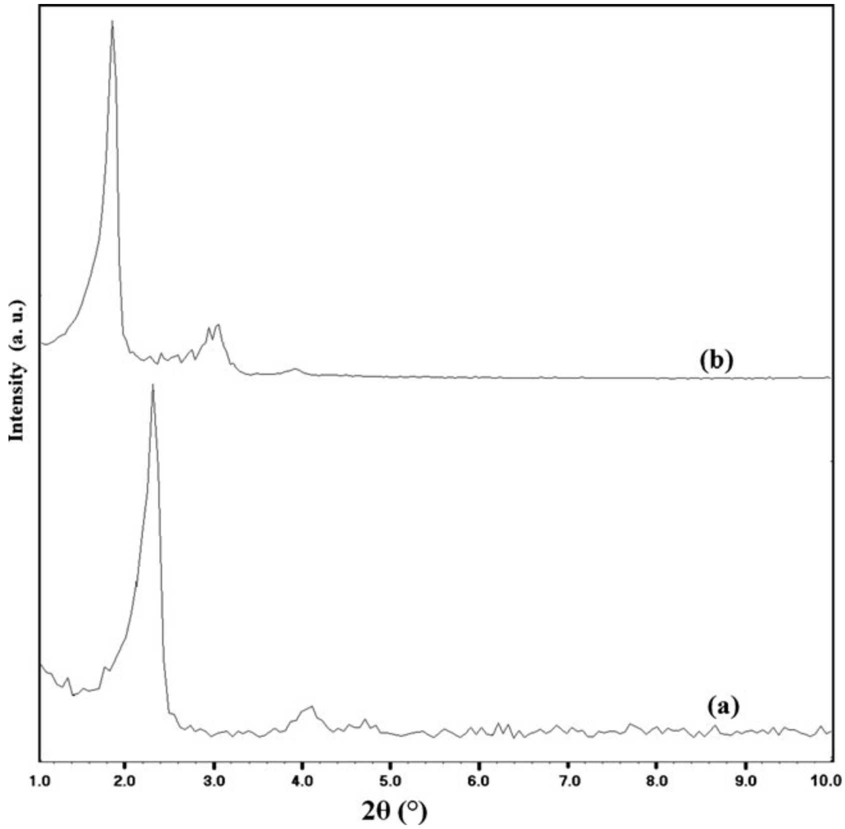

Fig. 2 The low-angle X-ray diffraction patterns of **a** py-MCM-41 and **b** py-MCM-48

triturated in a porcelain mortar. After sieving fractionated to a particular size the sizes less than 20 μm was dissolved in 10 mL of 3 mol L^{-1} HNO_3 solution and diluted with distilled water up to final volume of 100 mL. To validate the present method, one certified reference material NIST 1572 (*Citrus* leaves) was used and digested as described above. Finally, the pH of solution was adjusted to 7 and the proposed method was applied to separate and preconcentrate nickel ions from the real samples. To remove alkaline and earth alkaline ions, the column was washed with 20 mL of distilled water prior to elution.

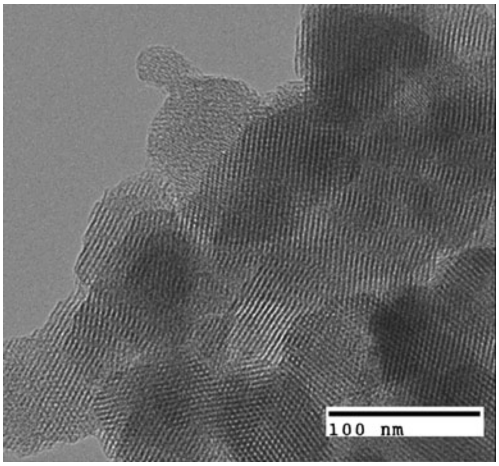

Fig. 3 The TEM micrograph of pyridine functionalized MCM-48

Column Preparation

A glass column, 120 mm in length and 20 mm in diameter, equipped with a porous disk was filled with a 200 mg of py-MCM-41 or py-MCM-48 nanoporous silica and was blocked with two polypropylene filters at the ends to avoid leakage of material during the course of sample loading. The bed height of nanoporous silica in the column was measured to be roughly 1 mm. To remove organic and inorganic contaminants, each glass column was washed with 5 mL of 1 mol L^{-1} hydrochloric acid, 5 mL of toluene, 5 mL of absolute ethanol, and 20 mL of distilled water.

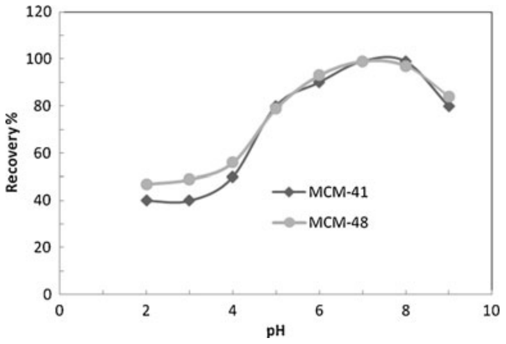

Fig. 4 Effect of pH of sample solutions on percent recovery of Ni(II) by py-MCM-41 and py-MCM-48. Conditions: sample concentration, 1 mg L^{-1}; sample volume, 100 mL; eluent, 6 mL of HCl 3 mol L^{-1}. Flow rate, 2 mL min^{-1}

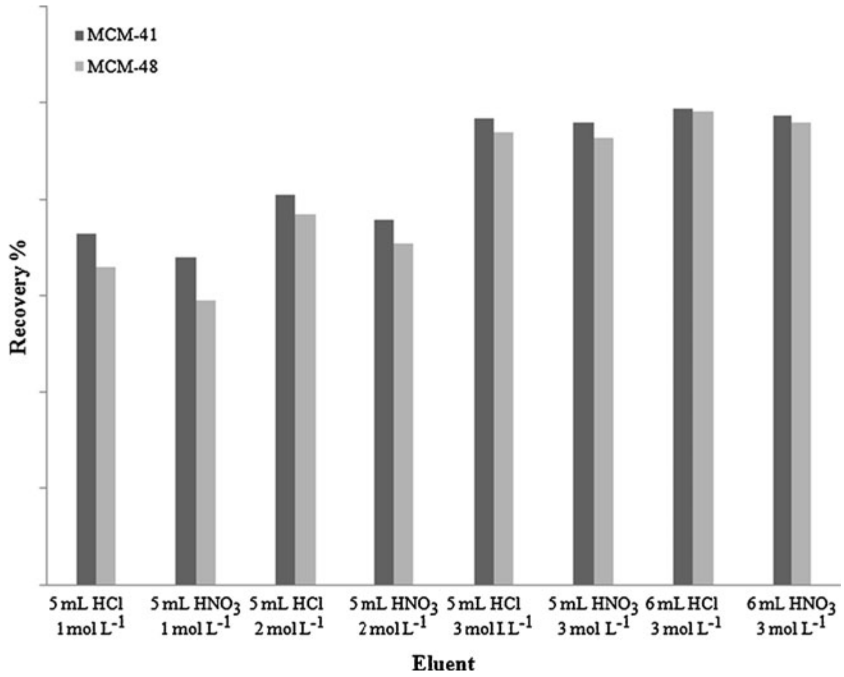

Fig. 5 Effect of type, concentration, and volume of eluent for desorption of Ni(II) by py-MCM-41 and py-MCM-48.Conditions: sample concentration, 1 mg L^{-1}; sample volume, 100 mL; pH=7; flow rate, 2 mL min^{-1}

Preconcentration Procedure

Aliquots with volume of 100 mL containing 1 μg mL^{-1} of nickel with pH of 7 were prepared. The pH was adjusted to 7 with the hydrogen phosphate/disodium hydrogen phosphate buffer solution. The column was preconditioned by passing 10 mL buffer solution. In light of the fact that flow rate is the single difference among the procedures for the two absorbents, the resulting solutions of nickel were passed through the column at previously optimized flow rates of 6 and 8 mL min^{-1} for py-MCM-41 and py-MCM-48, respectively. The retained Ni(II) ions were eluted with 6 mL of 3.0 mol L^{-1} HCl solution with flow rate of 2 mL min^{-1}. Nickel content was determined by FAAS. Five measurements were made for each sample and the results were averaged.

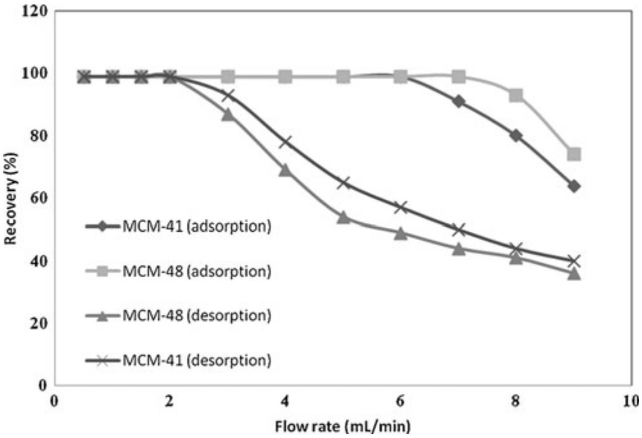

Fig. 6 Effect of flow rates of sample solutions on the percent recovery of Ni(II) by py-MCM-41 and py-MCM-48. Conditions: sample concentration: 1 mg L^{-1}; sample volume, 100 mL; pH=7; eluent, 6 mL of HCl 3 mol L^{-1}. Flow rate, 2 mL min^{-1}

Result and Discussion

Characterization of Pyridine Functionalized Nanoporous Silica

Syntheses of both nanoporous silica and pyridine-functionalized materials were confirmed by IR spectroscopy, low-angle X-ray diffraction, transmission electron microscopy (TEM) and elemental analysis. In the IR spectra of

Table 1 The tolerance limit of the diverse ions on the determination of nickel

Interfering ion	Tolerable concentration Ratio X/Ni	Py-MCM-41 R%±RSD	Py-MCM-48 R%±RSD
Na^+	3,000	99.0±1.3	98.0±1.9
K^+	3,000	99.5±0.4	98.5±0.6
Cs^+	1,500	98.5±1.1	95.0±1.3
Ca^{+2}	750	96.5±0.7	96.5±0.5
Mg^{+2}	750	93.5±1.0	93.0±1.1
Cr^{+3}	500	97.0±2.1	96.0±2.5
Cd^{+2}	500	93.0±2.9	94.5±3.2
Mn^{+2}	500	96.0±2.4	94.5±2.8
Pb^{+2}	300	92.0±3.8	95.0±3.8
Fe^{+2}	500	93.0±3.7	94.0±3.0
Zn^{+2}	750	98.5±1.5	97.0±1.7
Cu^{+2}	300	95.5±2.0	93.0±2.9
SO_4^{2-}	300	98.8±1.1	97.7±0.7
NO_3^-	3,000	97.6±2.1	96.4±1.6

Conditions: sample pH=7; sample volume, 100 mL; eluent, 6 mL of HCl 3 mol L^{-1} ; Sample flow rate, 6 and 7 mL min^{-1} for py-MCM-41 and py-MCM-48, respectively

Table 2 Comparison of adsorption capacities and detection limits of different common adsorbents

Solid support	Ligand	Limit of detection	Adsorption capacity (mg g^{-1})	Reference
MCM-41	N-[3-(triethoxysilyl) propyl]isonicotinamide	3.20 ng mL^{-1}	83.0	Present work
MCM-48	N-[3-(triethoxysilyl) propyl]isonicotinamide	3.50 ng mL^{-1}	85.5	Present work
Silica gel	Gallic acid	0.92 μg mL^{-1}	4.6	Sarkar et al. (2002)
	Salicyldoxime	1.50 μg mL^{-1}	2.4	Alan et al. (2007)
	o-Dihydroxybenzene	3.06 μg mL^{-1}	6.4	Tewari and Singh (2001)
Amberlite XAD-2	Pyrocatechol	0.24 μg mL^{-1}	4.1	Tokalıŏglu et al. (2006)
Amberlite XAD-4	Ammonium pyrrolidine Dithiocarbamate	0.40 μg mL^{-1}	7.21	Ramesh et al. (2002)
Cellulous	Pyrocatechol	5.51 μg mL^{-1}	8.7	Gurnani et al. (2003)

pyridine functionalized MCM-41 and MCM-48 silicas the starching vibrations of aromatic and aliphatic CH along with starching vibration of the carbonyl group unambiguously confirmed functionalization of MCM-41 and MCM-48 silicas with -$CH_2CH_2CH_2NHC(O)C_5H_4N$ group. The Si-O-Si stretching vibration of functionalize materials, py-MCM-41 and py-MCM-48, did not show significant change in comparison with bare silicas. Furthermore, the low-angle X-ray diffraction patterns of the functionalize materials (Fig. 2) in addition to TEM micrograph of MCM-48 (Fig. 3) demonstrated that the nanoporous structure after functionalization is maintained.

Optimization of Conditions

It is evident that extraction and preconcentration of metal ions such as Ni(II) on py-MCM-41 and py-MCM-48 is strongly dependent on conditions such as pH, eluent volume, concentration, flow rate of elution, and sample volume. Therefore, the aforementioned factors were optimized. The quantity of nickel adsorbed on solid phase was calculated in effluent and eluent solutions.

Effect of pH

Out of the parameters referred earlier, pH is deemed to be the most decisive parameter for adsorption of metal ions on py-MCM-41 and py-MCM-48. We are on the belief that selectivity of the above adsorbents can be manipulated by varying the pH of the solution. To assess the impact of pH on extraction efficiency, pH of 100 mL sample solutions containing 1 mg L^{-1} of nickel ions was adjusted in the range of 2–10. The retained Ni(II) ions were eluted with 10 mL of 3.0 mol L^{-1} HCl. FAAS was used to determine the amount of nickel ions in the eluent. The graph of recovery versus pH is shown in Fig. 4. As it is evident from this figure, quantitative recovery for both py-MCM-41 and py-MCM-48 is resulted in the pH range of 7–8. The progressive decrease in the retention of nickel ions at low pHs is due to the competition of the hydrogen ions with the nickel ions for binding to the pyridine group. Considering the safety and ease of operation at neutral pHs, pH=7 gets the upper hand here.

Effect of Type, Concentration, and Volume of Eluent

A series of selected eluent solutions such as HCl, HNO_3, and methanol in different concentrations were used to strip Ni(II) ions off of py-MCM-41 and py-MCM-48. We noticed that HCl solution with concentrations greater than 3.0 mol L^{-1} lead to effective elution of Ni(II) from py-MCM-41 and py-MCM-48 nanoporous silica. In this work, a 3.0 mol L^{-1} HCl solution was selected as eluent and the effect of eluent volume on the recovery of nickel was also studied (Fig. 5). Quantitative recovery can be obtained with 6 mL of 3.0 mol L^{-1} HCl solution. The same results were found for py-MCM-41 and py-MCM-48, under optimum

Table 3 Comparison of two mesoporous silicas MCM-41 and MCM-48

MCM	Sample flow rate	Pyridine loading (mmol g^{-1})	Recovery (%)	LOD[a] (ng mL^{-1})	RSD[b]	Maximum capacity (mmol g^{-1})	Preconcentration factor
Py-MCM-41	6	1.80	99.00	3.50	0.72	1.28	108
Py-MCM-48	7	1.83	98.50	3.25	1.50	1.45	108

[a] Limit of detection

[b] Relative standard deviation in 50 ng mL^{-1}

Table 4 Recovery of determination of nickel in certified reference materials

Sample	Solid phase	Concentration (mg kg^{-1})		Recovery (%)	Relative error (%)
		Certified	Found		
SRM 2710 (soil sample)	MCM-41	8.00±1.00	7.87±0.61	97.5	3.1
	MCM-48	8.00±1.00	8.06±0.82	100.7	1.7
SRM 2711 (soil sample)	MCM-41	21.70±0.70	21.39±0.42	98.6	2.2
	MCM-48	21.70±0.70	21.58±0.55	99.4	2.4
NIST 1572 (citrus leaves)	MCM-41	0.60±0.30	0.63±0.10	105.0	3.8
	MCM-48	0.60±0.30	0.64±0.12	106.6	4.0
DORM-2 (dogfish muscle)	MCM-41	19.4±3.1	20.01±0.30	103.1	2.5
	MCM-48	19.4±3.1	20.45±0.32	105.4	2.9

Condition: sample volume, 100 mL; pH sample, 7; eluent volume, 6 mL of HCl 3 mol L^{-1}; Sample flow rate, 6 and 7 for py-MCM-41 and py-MCM-48, respectively

conditions. Consequently, the volume of 6 mL of eluent for desorption of nickel was used in the following experiments.

Sample and Eluent Flow Rates

It is well established that the time of analysis and recovery relies highly on the flow rate of solution. Hence, the influence of sample and eluent flow rates upon recovery on py-MCM-41 and py-MCM-48 were studied. 100 mL solutions containing 1 μg mL^{-1} of Ni(II) were adjusted to pH=7 and was then passed through the column at flow rates ranging from 0.5 to 9 mL min^{-1} with a peristaltic pump. Subsequently, 6 mL of eluent was passed to desorb the bounded nickel ions from py-MCMs at flow rate of 2 mL min^{-1}. Apparently, as Fig. 6 shows, variation of the sample flow rate in the range of 1–6 mL min^{-1} has no effect on the elution efficiency of py-MCM-41 and py-MCM-48. The optimum flow rate for py-MCM-41 and py-MCM-48 were found to be 6 and 7 mL min^{-1}, respectively. The decline in absorption at higher flow rates can be attributed to the lack of equilibrium between the metal ions and py-MCMs. It seems that py-MCM-48 with an interconnected three-dimensional pore network can absorb metal ions at a higher clip than py-MCM-41 with its uniform one-dimensional pore network. On the other hand, the quantitative recoveries for desorption of nickel ions were obtained in the flow rate range of 0.5–2.0 mL min^{-1} for both py-MCM-41 and py-MCM-48 with 3 mol L^{-1} HCl solution; therefore, flow rate of 2.0 mL min^{-1} was chosen as optimum flow rate for elution process (Fig. 6).

Influence of Interference Ions

To study the effect of various naturally occurring anions (SO_4^{2-}, NO_3^{-}) and cations on the determination of nickel, various concentrations of Na^+, K^+, Cs^+, Mg^{+2}, Ca^{+2}, Cd^{+2}, Fe^{+2}, Mn^{+2}, Pb^{+2}, and Cr^{+3} ions were added as their chloride salts to 100 mL aliquots of solutions containing nickel in ratios that are listed in Table 1. After applying the proposed method, the tolerance amount of each ion was determined. The tolerance amount was defined as the maximum concentration found to cause a change in signal that is less than 5% compared with the signal for nickel alone. As indicated in Table 1, at neutral pH, most transition metals cause no interference whatsoever at concentrations found in nature and the method is selective toward nickel at pH=7. Since the method described is not affected by relatively high concentrations of alkaline and alkaline earth metals, the presented method can

Table 5 Recovery and precision of the determination of nickel in various environmental water samples

Sample	Real sample (ng mL^{-1})		Added (ng mL^{-1})		Found (ng mL^{-1})		Recovery (%)	
	MCM-41	MCM-48	MCM-41	MCM-48	MCM-41	MCM-48	MCM-41	MCM-48
Distilled water	0.00	0.00	5.00	5.00	4.95±0.10	4.92±0.10	99.00	98.50
Tap water	0.00	0.00	5.00	5.00	4.81±0.06	4.87±0.09	96.20	97.40
River water	41.00	40.00	40.00	40.00	75.00±0.20	77.00±0.40	92.59	95.06
Sea water	68.9	70.03	60.00	60.00	133.3±3.2	135.9±2.6	103.41	104.51

Condition: sample volume, 100 mL; pH sample, 7; eluent volume, 6 mL of HCl 3 mol L^{-1} ; Sample flow rate, 6 and 7 for py-MCM-41 and py-MCM-48, respectively

Table 6 The concentration of nickel in soil samples with different distance with Petrochemical Company

Distance (km)	Mean ($mg\ kg^{-1}$)		Minimum ($mg\ kg^{-1}$)		Maximum ($mg\ kg^{-1}$)	
	MCM-41	MCM-48	MCM-41	MCM-48	MCM-41	MCM-48
10	73.7	75.5	50.3	55.8	90.5	89.8
15	75.8	75.4	49.6	50.3	88.2	91.0
20	58.6	61.9	50.0	49.1	76.3	79.7
25	39.1	41.2	38.8	39.3	45.2	44.9
30	40.4	39.7	37.5	36.3	44.8	42.2

Condition: sample volume, 100 mL; pH sample, 7; eluent volume, 6 mL of HCl 3 mol L^{-1}; Sample flow rate, 6 and 7 for py-MCM-41 and py-MCM-48, respectively

be applied to various samples, including sea water and samples containing nickel at the concentration in the ppb level.

Maximum Adsorption Capacity

The maximum capacity of py-MCM for Ni(II) was established by passing 500 mL portions of aqueous solutions containing 100 mg of nickel through the column. Considering the 1:1 reaction ratio of Ni(II) with active sites of pyridine, the maximum capacity of py-MCM-41 obtained for three replicates was found to be 83.00 mg g^{-1} (1.28 mmol g^{-1}) of Ni(II). For the sake of comparison, the same adsorption experiments were carried out with py-MCM-48, and a maximum capacity of 85.50 mg g^{-1} (1.45 mmol g^{-1}) of Ni(II) was obtained for five replicates.

Dilution and Kinetic Effect

Of the nickel, 1.0 mg was dissolved in 100, 200, 500, 1,000, 1,500, and 2,000 mL of distilled water to determine the break through volume of the method. Nickel ions were quantitatively eluted from 2,000 mL of sample solution. Thus, the breakthrough volume for the proposed SPE method on py-MCM-41 and py-MCM-48 should be greater than 2,000 mL.

The enrichment factor was established using the recommended column procedure by employing increasing volumes the effect of 1 μg mL^{-1} Ni(II) solutions. For this reason, 10–800 mL of Ni(II) solution was passed on the MCMs. Maximum sample volume was found to be 650 mL with recovery being greater than 98%. At higher volumes, the recoveries for Ni(II) was not quantitative. Thus, enrichment factors as high as 108 on py-MCM-41 were obtained as the ratio of the highest sample volume (650 mL) and the lowest eluent volume (6 mL). The same result was obtained for py-MCM-48.

Figures of Merit

Being one the most crucial parameter by which a method is evaluated, the detection limit of the proposed method was determined by passing 500 mL blank solutions for ten times through the column under the optimal experimental conditions. The values of limit of detection (LOD) for nickel on py-MCM-41 and py-MCM-48 were 3.50 and 3.25 ng mL^{-1}, respectively. These results were obtained from $C_{LOD}=kS_b/m$; where, $k=3$ and the amount of slope of the calibration curve (meter), was obtained from the equation of Ni extraction ($y=5.5886x+0.4943$ for MCM-41 and $y=6.0186x+0.5076$ for MCM-48; Xie et al. 2008). Table 2 offers a comparison with rival methods.

The other factor being of high importance is precision. The precision of the method under optimum conditions was determined by performing ten replicates. The recoveries were found to be 99.00%±0.72 and 98.50%±1.50 on py-MCM-41 and py-MCM-48, respectively.

Two solid phases (py-MCM-41 and py-MCM-48) were compared with each other and the results are shown in

Table 7 The concentration of nickel in fish and plant samples

Fish	Mean ($mg\ kg^{-1}$)		Minimum ($mg\ kg^{-1}$)		Maximum ($mg\ kg^{-1}$)	
	MCM-41	MCM-48	MCM-41	MCM-48	MCM-41	MCM-48
Flounder Fish	0.379	0.383	0.250	0.265	0.551	0.537
Lion fish	0.351	0.347	0.272	0.277	0.514	0.543
Stromateus cinereus	0.406	0.411	0.310	0.323	0.622	0.619
Zataria multifloria Boiss	4.41	4.48	3.54	3.48	5.07	5.13
Apocynaceae	2.79	2.90	2.01	2.14	3.00	3.02
Citrullus colocynthis	3.66	3.51	2.95	3.00	4.18	4.21

Condition: sample volume, 100 mL; pH sample, 7; eluent volume, 6 mL of HCl 3 mol L^{-1}; sample flow rate, 6 and 7 for py-MCM-41 and py-MCM-48, respectively

Table 3. At the first glance, it seems that py-MCM-48 can be more effective for Ni(II) extraction than py-MCM-41 because its maximum capacity is more at higher flow rate than py-MCM-48. But as can be seen from Table 3, py-MCM-48 has lower recovery with higher RSD than py-MCM-41.

Validation of the Method

Three certified materials NSC DC 73323 (soil), DORM-2 (*Dogfish muscle*), and NIST 1572 (*Citrus* leaves) were used for validation of the proposed method. As Table 4 shows, a good correlation was obtained between the estimated content and the one found by the proposed method. Therefore, both MCM-41 and MCM-48 can be used as a confident solid-phase for extraction and determination of nickel in different kinds of samples (soil, vegetables and animal tissue). The results show that the present method for nickel is not affected by potential interferences from major matrix elements of the analyzed soil, vegetables, and animal tissue samples.

Determination of Nickel in Real Environmental Samples

In order to investigate the applicability of this method, different kinds of real samples were analyzed. With these analyses, the effect of different matrices on the method was studied. To reduce the effect of complex matrices of environmental samples, modified nanoporous material was applied as a selective sorbent for nickel extraction in pH 7. In this case, the amount of Ni(II) was less than the detection limit of the instrument, we spike extra amounts of Ni(II) so we to be able carry out this experiment out in a real matrix. For sample preparation, certain amounts of Ni(II) were spiked (Table 5, 6, and 7). As shown, in all cases, the recovery is almost quantitative.

Conclusion

The proposed method provides an effective approach towards preconcentration of Ni(II) ions in aqueous solutions. The method is simple, rapid and reliable by comparison with rival methods. The analytical performance and figures of merit, namely relative standard deviation, limit of detection, and recovery for this method are either better or comparable to other methods and involves a minimal usage of solvents and chemicals that are not environmentally friendly. The high preconcentration factor and precision of this method as well as its satisfactory reproducibility makes it applicable to aqueous solutions in which their nickel content is below the detection limit of FAAS.

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