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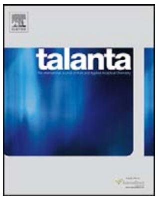

Determination of very low levels of gold and palladium in wastewater and soil samples by atomic absorption after preconcentration on modified MCM-48 and MCM-41 silica

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ABSTRACT

A simple and rapid method was applied for extraction, preconcentration and determination of trace amounts of gold and palladium in wastewater by using functionalized mesoporous silica. Extraction was investigated on adsorbents prepared by grafting aminopropyl on the surface of MCM-41 and MCM-48 mesoporous silica. The optimum experimental conditions such as pH, flow rates, type and the smallest amount of eluent for elution of Au and Pd, break through volume and the influence of various cationic interferences on the sorption of gold(III) and palladium(II) were evaluated. The extraction efficiency for gold and palladium were greater than 98% and limit of detection (LOD) was lower than 0.06 ng mL^{-1} for gold and 0.1 ng mL^{-1} for palladium on both functionalized MCM-41 and MCM-48 silica. The preconcentration factor was greater than 800 for gold and 400 for palladium and the relative standard deviation (RSD) of the method was <1%. The adsorption capacity of the mesoporous silica was greater than 285 mg g^{-1} for Au and 145 mg g^{-1} for Pd on both functionalized MCM-41 and MCM-48 silica. The results of MCM-41 were compared with those of MCM-48 under similar experimental conditions, the results show that flow rate was the single point of difference among the procedures. MCM-48 has similar recovery to MCM-41 at higher flow rates only under identical conditions. The proposed method was applied for the determination of gold(III) and palladium(II) in some real samples, including wastewater and soil samples.

1. Introduction

There is great interest in the removal and recovery of precious metals such as gold, palladium, platinum and other noble metals from wastewater. The two most important reasons and motivations for precious metal removal are the economical impact of losing these metals and their environmental concerns [1]. Trace amounts of these precious metals can be found in some wastewaters as a result of mining [2], electroplating industries [3], or electronic and jewellery manufacturing. Removal and recovery of noble metals from these manufacturing wastewaters for reuse can be financially beneficial and definitely decreases the production costs. Concentration of precious metals in environment and wastewaters are usually low, thus, an effective separation and preconcentration process prior to determination is an essential step.

Many techniques are available for the separation and preconcentration of precious metals from wastewater, such as solvent extraction [4], membrane disk [5,6], ion-exchange [7], coprecipitation [8,9], cloud point extraction [10], electrodeposition [11], leaching [12], chlorination [13], cyanidation [14], and adsorption processes [15]. Each method has its own advantages and disadvantages. For example solid phase extraction (SPE) based on an adsorption mechanism has been widely used for preconcentration of precious metals. This method is simple, rapid and efficient with high preconcentration factor compared to the other separation techniques.

Over the past few years, in a considerable number of studies, several selective adsorbents, such as chitosen [15], activated carbon [16], Dowex M 4195 [17], chitin [18], micro-beads [19], thiol cotton fiber [20], chelating fiber [21], ion-imprinted polymers (IIPs) [22], hydrogel [23], modified resin [24], polyurethane foam [25], activated alumina [26] and modified silica [27–29] have all been used for the removal of noble metal ions. In recent years, after the discovery of the mesoporous family of silica (M41S) by Beck et al. [30], chemically modified silica has attracted great attention for metal removal because of several major advantages, such as homogeneous surface property, narrow pore size distribution and large surface area, which enables high adsorption capacities. Mesoporous silicas, with their chemically modified surface, have been extensively used in catalysis [31], nanotechnology [32] and

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biotechnology [33]. Recently, chemically modified mesoporous silicas have also been used as an adsorbent for various compounds such as dyes [34], organic compounds [35], cations and anions [36], aromatic hydrocarbons [37] and metal ions [38], from aqueous solutions.

A review of the literature shows that the majorities of studies have been based on hexagonal-phase mesoporous silica (MCM-41) with a uniform two-dimensional pore network. There are a limited number of studies on MCM-48 with three-dimensional and cubic pore system as an adsorbent. Until now, MCM-48 mesoporous silica has only been used as an adsorbent in a few studies involving some gases [37], dyes [34] and heavy metals [38]. This work describes adsorption of trace amounts of gold and palladium ions from real samples using the surface-modified MCM-41 and MCM-48 mesoporous silica (Mobil Composite Material No. 41 and 48). The effects of various analytical parameters on the extraction efficiency of Au(III) and Pd(II) such as pH, flow rates, type and the smallest amount of eluent for elution of Au and Pd, break through volume, adsorption capacity and the influence of various cationic interferences were investigated. The proposed method was applied for the determination of Au and Pd in real samples.

2. Experimental

2.1. Reagents and solutions

All reagents used in this study were analytical grade. Pd(II) and Au(III) standard solutions with concentration of 1000 μg mL^{-1} were purchased from Merck (Darmstadt, Germany). The working solutions of Pd and Au were obtained by appropriate dilution of the stock solutions with buffer solutions. The required pH adjustments were made with buffer solutions. For pH 1–4, $Na_3C_3H_5O(CO_2)_3/HCl$ (trisodium citrate/hydrochloric acid) buffer solutions were used. The $CH_3COOH/NaCH_3COO$ buffer solutions were used to adjust pH in the range of 4–6, while Na_2HPO_4/NaH_2PO_4 buffer solutions were used for pH 6–10. All required solutions were prepared using deionized water, provided from a Milli-Q (Millipore, Bedford, MA, USA) purification system. Thiourea, thioacetamide, CH_3COOH, $Na_3C_3H_5O(CO_2)_3$, Na_2HPO_4, NaH_2PO_4, HCl and HNO_3 were purchased from Merck and used without further treatment. MCM-41 and MCM-48 were prepared according to earlier reports [39,40] and were then functionalized by 3-aminopropyltriethoxysilane [41]. For the functionalization of mesoporous silicas, 1 g of MCM-41 or MCM-48 was suspended in 50 mL toluene and the mixture was stirred for 1 h. To this solution was then added 1.6 g of $(C_2H_5O)_3Si(CH_2)_3NH_2$ and reaction heated at reflux temperature for 2 h. The white solid was removed from the solvent by filtration, washed with toluene and chloroform and then dried at room temperature. Functionalized MCM-41 and MCM-48 are designated as NH_2-MCM-41 and NH_2-MCM-48, respectively. An amine loading of 2.53 and 2.74 mmol amine/g of mesoporous silica was obtained for NH_2-MCM-41 and NH_2-MCM-48 as found by carbon and nitrogen analysis.

2.2. Instruments

All absorbance measurements were carried out on a Shimadzu AA-680 atomic absorption spectrometer using an air/acetylene flame. Au and Pd hallow cathode lamps from Shimadzu served as the radiation source at wavelengths of 242.8 and 244.8 nm for Au and Pd, respectively. The pH measurements were made at 25 ± 1 °C with a digital WTW Metrohm 827 Ion analyzer (Switzerland) equipped with a combined glass–calomel electrode. A vacuum pump was obtained from Leybold (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 extraction. A Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

2.3. Procedure

2.3.1. Column procedure

A glass column (120 mm in length and 2 cm in diameter) with a porous disk was packed with a mixture of 200 mg of NH_2-MCM-41 or NH_2-MCM-48 and blocked by two polypropylene filters at the ends to prevent loss of the mesoporous material during sample loading. In order to decrease time of extraction, the bed height of the mesoporous silica in the column was adjusted to approximately 1 mm. In order to remove organic and inorganic contaminants, and precondition the bed prior to extraction, each glass column was washed with 5 mL of 1 mol L^{-1} hydrochloric acid, 5 mL of absolute ethanol, 5 mL of toluene and 20 mL of distilled water. The column was stable up to 10 adsorption/elution cycles without an obvious decrease in the recovery of gold and palladium ions. In order to reactivate after 10 cycles, the column was washed with 10 mL of 2 mol L^{-1} regia water, 5 mL of absolute ethanol and 5 mL of toluene and finally 20 mL of distilled water. The column was then kept in an oven for 6 h at 40 °C.

2.3.2. Preconcentration procedure

100 mL of each sample solution containing 1 μg mL^{-1} of gold or palladium at a pH of 3 or 7, respectively, were prepared. The pH was adjusted to 3 and 7 for gold and palladium ions using $Na_3C_3H_5O(CO_2)_3/HCl$ and Na_2HPO_4/NaH_2PO_4 buffer solutions, respectively. The column was preconditioned by passing the buffer solution through the column for several minutes. The resulting solutions of gold and palladium were passed through the column containing NH_2-MCM-41 at a flow rate of 8 mL min^{-1} for gold and 6 mL min^{-1} for palladium. The retained Au(III) and Pd(II) ions were eluted with 9 and 7 mL of 0.1 mol L^{-1} thiourea solution in 3 mol L^{-1} HCl solution, respectively. The same procedure was repeated for palladium and gold with NH_2-MCM-48 at a flow rate of 12 and 8 mL min^{-1}. Au and Pd content in the eluent were determined by FAAS with five measurements made for each sample and the results were averaged.

2.3.3. Sample preparation

The water samples were obtained from a tap (Tehran, Iran) and the wastewater from a jewellery manufacturing firm (Tehran, Iran) and soil sample was collected from city of Qazvin (Iran). Standard material sample (NCS DC 73323) with a certified gold content, was obtained from the China National Analysis Center for Iron and Steel. The water samples were collected in cleaned polyethylene bottles and filtered through 0.45 μm pore size nylon filters (Millipore) immediately after sampling. The pH of the samples was adjusted to 3 and 7 by addition of $Na_3C_3H_5O(CO_2)_3/HCl$ and Na_2HPO_4/NaH_2PO_4 buffer solutions for Au and Pd, respectively. Finally, the proposed method was applied for preconcentration of gold and palladium ions from the water samples. To remove alkaline and earth alkaline ions, the column was washed with 20 mL of distilled water prior to elution. 1000 mg of soil was 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 to 50.0 mL with deionized water [42]. At the same time, standard material was digested according to the above digestion method, as well as, a blank digestion. The preconcentration procedure detailed above was then applied to the final solutions.

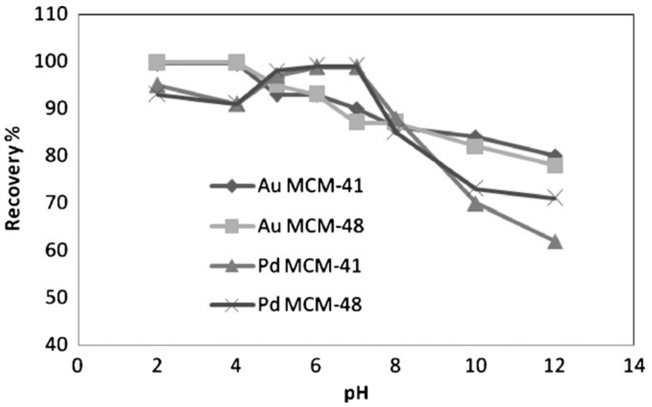

Fig. 1. Effect of pH of sample solutions on percent recovery of Pd(II) and Au(III) by MCM-41 and MCM-48. Conditions: Pd and Au, $1\,\mu g\,mL^{-1}$; sample volume, 100 mL; sample flow rate, $5\,mL\,min^{-1}$; eluent, 10 mL of thiourea $0.1\,mol\,L^{-1}$ in HCl solution $3\,mol\,L^{-1}$; eluent flow rate, $2\,mL\,min^{-1}$.

3. Results and discussion

It is well known that extraction and preconcentration of precious metals, such as Au and Pd, from nature is very important. Therefore, to obtain quantitative recoveries of gold and palladium ions on NH_2-MCM-41 and NH_2-MCM-48, the SPE procedure was optimized for various analytical parameters. The percentages of Au(III) and Pd(II) adsorbed on mesoporous silica were calculated from the amount of gold and palladium ions in the effluent and eluent solutions obtained by applying the general procedure.

3.1. Effect of pH

Among the tested variables, pH was found to be the most critical parameter for adsorption of metals on the mesoporous silica. In order to evaluate the effect of pH on the extraction efficiency, the pH of the 100 mL sample solutions containing $1\,\mu g\,mL^{-1}$ of gold and palladium ions was adjusted to fit in the range of 2–12. The retained Pd(II) and Au(III) ions were then eluted with 10 mL of $0.1\,mol\,L^{-1}$ thiourea in $3\,mol\,L^{-1}$ HCl. Pd and Au ions content in the eluent was determined by FAAS and the data graphed as a function of pH, are shown in Fig. 1. As it can be seen, quantitative recovery ($\geq$99%) for both NH_2-MCM-41 and NH_2-MCM-48 were obtained in the pH range of 2–4 and 6–7 for Au and Pd, respectively. Adsorption of gold ions from strongly acidic solutions was an advantage because strong acids are usually used to decompose many materials including gold.

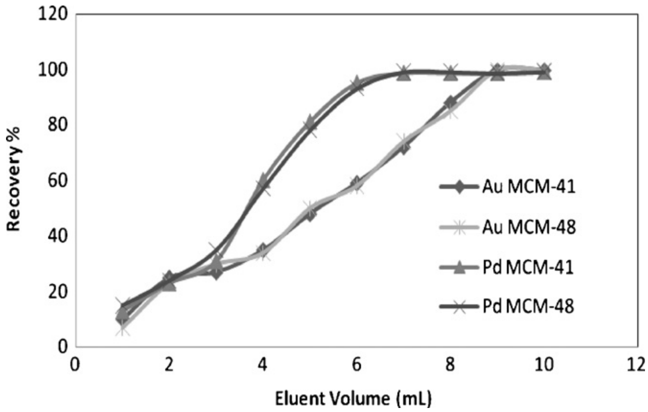

Fig. 2. Effect of eluent volume on percent recovery of Pd(II) and Au(III) by NH_2-MCM-41 and NH_2-MCM-48. Conditions: Pd and Au, $1\,\mu g\,mL^{-1}$; sample volume, 100 mL; sample flow rate, $5\,mL\,min^{-1}$; pH sample 3 and 7 for Au and Pd; eluent, thiourea $0.1\,mol\,L^{-1}$ in HCl solution $3\,mol\,L^{-1}$; eluent flow rate, $2\,mL\,min^{-1}$.

3.2. Effect of type, concentration and volume of eluent

In order to desorb Au(III) and Pd(II) ions from the mesoporous silica, a series of selected eluent solutions, such as HCl, HNO_3, thiourea, thioacetamide and methanol, were used at different concentrations. As shown in Table 1, the recoveries of gold and palladium ions were not quantitative when HCl, HNO_3, thioacetamide or methanol were used alone as the eluent. It was eventually found that $0.1\,mol\,L^{-1}$ thiourea in $3\,mol\,L^{-1}$ HCl solution provided effective elution of Au(III) and Pd(II) from amino-functionalized mesoporous silica (NH_2-MCM-41 and NH_2-MCM-48).

The effect of eluent volume on the recovery of gold and palladium ions was also studied (Fig. 2). As Fig. 2 shows, quantitative recovery could be obtained with 7 or 9 mL of $0.1\,mol\,L^{-1}$ thiourea in a $3\,mol\,L^{-1}$ HCl solution for palladium or gold, respectively. At optimal conditions, these same results were found for NH_2-MCM-41 and NH_2-MCM-48. Therefore, volumes of 7 and 9 mL of eluent for the desorption of Au and Pd were used in the remaining experiments.

3.3. Sample and eluent flow rates

The time of analysis and the recovery of the adsorption are very important factors, and they depend on the flow rate of the tested solution. Therefore, the effect of flow rates of sample and eluent solutions from NH_2-MCM-41 and NH_2-MCM-48 on the retention and recovery of Au and Pd ions was studied. To determine the aforementioned factors, 100 mL of $1\,\mu g\,mL^{-1}$ Au(III) and Pd(II) solu-

Table 1
Effect of type of eluent on percent recovery of Pd(II) and Au(III) by NH_2-MCM-41 and NH_2-MCM-48.

Eluent	MCM-41 (Au) R[a]% ± S[b]	MCM-48 (Au) R% ± S	MCM-41 (Pd) R% ± S	MCM-48 (Pd) R% ± S
HNO_3 1 ($mol\,L^{-1}$)	37.5% ± 2.0	35.0% ± 1.5	42.8% ± 3	40% ± 2
HNO_3 2 ($mol\,L^{-1}$)	41.8% ± 2.5	39% ± 4	44% ± 1	44.4% ± 2.5
HNO_3 3 ($mol\,L^{-1}$)	53% ± 1	48.2% ± 2.0	53% ± 2	49.5% ± 3.0
HCl 1 ($mol\,L^{-1}$)	55.3% ± 1.5	57.0% ± 0.5	60.7% ± 0.5	57.5% ± 2.5
HCl 2 ($mol\,L^{-1}$)	61.7% ± 3.0	61% ± 1	68% ± 2.5	63% ± 1
HCl 3 ($mol\,L^{-1}$)	65.0% ± 3.5	68.0% ± 2.5	72.1% ± 1	69% ± 3
HNO_3 2 ($mol\,L^{-1}$) + HCl 2 ($mol\,L^{-1}$)	60.5% ± 1.0	61.7% ± 3.0	64% ± 2	62.2% ± 1.5
HNO_3 1 ($mol\,L^{-1}$) + HCl 2 ($mol\,L^{-1}$)	61.4% ± 4	62.5% ± 1.5	66.3% ± 1.5	65% ± 4
Thioacetamide 1 ($mol\,L^{-1}$) + HCl 3 ($mol\,L^{-1}$)	64% ± 2	64.5% ± 1.0	65% ± 1.5	63% ± 2
Thiourea 0.1 ($mol\,L^{-1}$) + thioacetamide 0.1 ($mol\,L^{-1}$)	75% ± 1	74.3% ± 1.5	81.4% ± 0.5	79% ± 2
Thiourea 0.5 ($mol\,L^{-1}$) + HCl 3 ($mol\,L^{-1}$)	99.9% ± 1.5	99.5% ± 1.0	99.1% ± 2	100.1% ± 2.5
Thiourea 0.1 ($mol\,L^{-1}$) + HCl 3 ($mol\,L^{-1}$)	99.8% ± 0.5	99.7% ± 0.7	98.7% ± 1	99.0% ± 0.5
Thiourea 0.1 ($mol\,L^{-1}$) + HCl 2 ($mol\,L^{-1}$)	98.0% ± 0.1	94% ± 3	95% ± 1	94.0% ± 2.5

Pd and Au, $5\,\mu g\,mL^{-1}$; sample volume, 50 mL; pH sample 3 and 7 for Au and Pd; sample flow rate, $5\,mL\,min^{-1}$; eluent flow rate, $2\,mL\,min^{-1}$; replicates number, 5.

[a] Recovery.

[b] Standard deviation.

Table 2
The tolerance limit of the diverse ions on the determination of palladium.

Interfering ions	Concentration (mg)	R[a]% ± S[b]			
		MCM-41 Au	MCM-48 Au	MCM-41 Pd	MCM-48 Pd
Na^+	500	98 ± 2	99 ± 3	97 ± 3	98 ± 3
K^+	250	100 ± 2	99 ± 3	98 ± 1	99 ± 2
Cs^+	150	99 ± 1	99 ± 2	97 ± 4	98 ± 2
Ca^{2+}	100	98 ± 1	100 ± 1	99 ± 3	101 ± 2
Mg^{2+}	100	97 ± 4	98 ± 2	95 ± 4	97 ± 3
Cd^{2+}	25	97 ± 1	99 ± 2	98 ± 4	99 ± 3
Ni^{2+}	6	99 ± 2	97 ± 1	94 ± 3	96 ± 2
Cu^{2+}	5	98 ± 1	97 ± 2	96 ± 2	96 ± 2
Cr^{3+}	25	96 ± 4	95 ± 4	93 ± 3	95 ± 1
Fe^{2+}	25	99 ± 2	98 ± 1	98 ± 3	100 ± 1

Pd and Au, 1 μg mL^{-1}, pH for Au and Pd 3 and 7; sample volume, 100 mL; eluent, 9 and 7 mL of thiourea 0.1 mol L^{-1} in HCl solution 3 mol L^{-1} for Au and Pd; sample flow rate, 8 and 6 mL min^{-1} for Au and Pd on NH_2-MCM-41 and 12 and 8 mLmin^{-1} on NH_2-MCM-48; eluent flow rate, 2 mL min^{-1}.

[a] Recovery.

[b] Standard deviation.

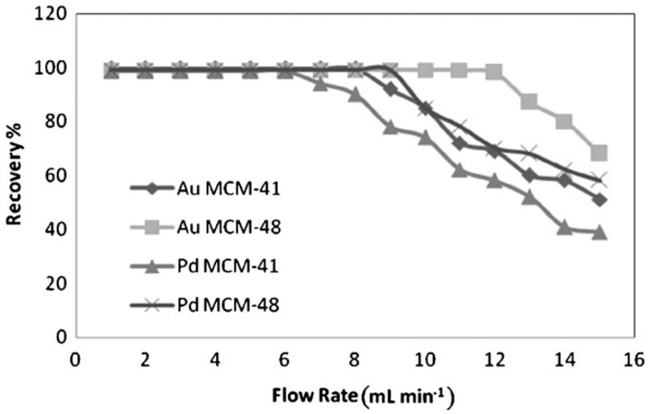

Fig. 3. Effect of flow rates of sample solutions on the percent recovery of Pd(II) and Au(III) by NH_2-MCM-41 and NH_2-MCM-48. Conditions: Pd and Au, 1 μg mL^{-1}; sample volume, 100 mL; pH sample 3 and 7 for Au and Pd; eluent volume, 9 and 7 mL of thiourea 0.1 mol L^{-1} in HCl solution 3 mol L^{-1} for Au and Pd.

Table 3
Adsorption capacity for gold of different common adsorbents.

Sorbent	Adsorption capacity (mg/g)	Reference
NH_2-MCM-41	285.0	This work
NH_2-MCM-48	305.0	This work
NRH-MCM-41	65.0	[44]
NR_2-MCM-41	40.0	[44]
Thioethetic site, silica gel	195.0	[28]
2-Mercaptobenzothiazole, silica gel	4.5	[29]
Cationic exchange resin	243.0	[24]
Dowex M 4195	8.1	[17]
Diol, poly(p-CMS-DVB) micro-beads	97.5	[41]
Activated carbon	35.0	[45]
Chitosan, magnetic nano-adsorbent	59.5	[15]
L-Lysine, chitosan resin	70.3	[46]

tions, adjusted to pH 3 and 7, respectively, were passed through the column with a peristaltic pump at flow rates in the range of 1–15 mL min^{-1}. The column was then washed with 20 mL of water to remove free metal ions, and 9 mL of eluent was passed through the column to desorb the bound gold ions and 7 mL for palladium from both NH_2-MCM-41 and NH_2-MCM-48 at a flow rate of 1 mL min^{-1}. The results of these studies are shown in Fig. 3. Variation of the sample flow rate in the range of 1–8 mL min^{-1} for Au(III) and 1–6 mL min^{-1} for Pd(II) had no effect on the elution efficiency in NH_2-MCM-41. The flow rate increased to 12 and 9 mL min^{-1} in NH_2-MCM-48 for Au(III) and Pd(II), respectively. On the other hand, quantitative recoveries for gold and palladium ions were obtained at a flow rate range of 0.5–2.0 mL min^{-1} for both NH_2-MCM-41 and NH_2-MCM-48 with 0.1 mol L^{-1} thiourea in a 3 mol L^{-1} HCl solution. The decrease in the percentage of adsorption at flow rates higher than the optimum was probably because Pd(II) and Au(III) do not equilibrate sufficiently with the NH_2-MCM-41 and NH_2-MCM-48 silica. As shown in Fig. 3, at higher flow rates, NH_2-MCM-48 with an interconnected three-dimensional pore network could adsorb metal ions faster than NH_2-MCM-41 with a uniform two-dimensional pore network.

3.4. *Influence of interfering ions*

In order to study selective separation, the effect of various cations found in natural samples on the determination of Pd(II) and Au(III) from binary mixtures was examined. Different concentrations of Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Cd^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+} and Cr^{3+} were added individually as their chloride salts to 100 mL of solution containing 0.1 mg of Pd(II) and Au(III), and the recommendation procedure for extraction of Au and Pd on mesoporous silica (41, 48) was followed. The tolerable amount was defined as the maximum concentration found to cause a change in the recovery of gold and palladium extraction that was <7%, as compared to the recovery for both metal ions alone. As given in Table 2, high concentrations of all the added ions did not interfere with the separation and determination of Pd(II) and Au(III). The results clearly showed that Au

Table 4
The limit of detections, regression equations, correlation of determinations for Au and Pd.

Metal ion	MCM-NH_2	Regression equation	r^{2a}	LOD[b] (ng mL^{-1})	RSD[c]%
Au (III)	MCM-41	$A = 6.099C + 0.067$	0.997	0.056	0.7
	MCM-48	$A = 6.167C + 0.068$	0.998	0.045	0.5
Pd (II)	MCM-41	$A = 2.700C + 0.031$	0.998	0.095	1
	MCM-48	$A = 2.842C + 0.030$	0.998	0.086	0.5

[a] Correlation coefficient.

[b] Limit of detection.

[c] Relative standard deviation.

and Pd ions in the ppm range in binary mixtures of diverse ions were retained more than the alkaline and alkaline earth metal ions on the column. The proposed method can, therefore, be applied to real samples, including sea water, and samples containing gold and palladium metals at μg L^{-1} level, since this study has demonstrated that high concentrations of alkaline and earth alkaline ions do not affect the analysis.

3.5. *Adsorption capacity*

The capacity of NH_2-MCM-41 and NH_2-MCM-48 for adsorption of Au(III) and Pd(II) was studied by passing 500 mL portions of aqueous solutions containing 100 mg of gold or palladium ions at optimal pH through the column. This was followed by determination of the effluent and retained metal ions using FAAS. The capacity of NH_2-MCM-41, obtained for five replicate analyses, was found to be 1.45 ± 0.03 and 1.37 ± 0.05 mmol g^{-1} of Au(III) and Pd(II), respectively (Table 3). Au(III) and Pd(II) can react with the active sites of the amines at a 1:1 ratio, based on ligand content on the sorbent. For comparison purposes, the same adsorption experiments were carried out with NH_2-MCM-48, and the adsorption capacities were found to be 1.55 ± 0.04 and 1.45 ± 0.03 mmol g^{-1} of Au(III) and Pd(II) for five replicate analyses, respectively. Similar adsorption capacities due to similar amine loading, were observed for both mesoporous silicas. It should be mentioned, however, that there was a higher flow rate and, consequently, faster analysis time for NH_2-MCM-48 in comparison with NH_2-MCM-41. This observation can be explained by the three-dimensional and cubic pore structure of NH_2-MCM-48.

3.6. *Analytical performance*

The break through volume of sample solutions was investigated by dissolving 10 μg of gold and palladium in 100, 200, 500, 1000, 1500, 2000 and 2500 mL of distilled water, and then following the proposed procedure. The Au and Pd ions were quantitatively retained from the 2500 mL and smaller volumes. Thus, the break through volume for the proposed SPE method for both metal ions with NH_2-MCM-41 and NH_2-MCM-48 should be greater than 2500 mL.

The enrichment factor was studied by performing the recommended column procedure using the higher volume 1 μg mL^{-1} solutions of Au(III) and Pd(II). The maximum sample volume was found to be 2500 mL for Au and 1250 mL for Pd; and by controlling the Au(III) and Pd(II) concentration in the effluents, a recovery of above 99.5% was achieved. The loaded gold and palladium ions were easily desorbed with 9 or 7 mL of 0.1 mol L^{-1} thiourea prepared in 3 mol L^{-1} HCl, depending on the metal ion, and then the volume was reduced to 3 mL by boiling. Thus, the high enrichment factors of 833 for Au and 417 for Pd for NH_2-MCM-48 were obtained. For comparison the same experiments were carried out with NH_2-MCM-48, and enrichment factors of 842 for Au and 438 for Pd were obtained. In order to determine the limit of detection (LOD) of the proposed method, 500 mL portions of a blank solution (n = 10) were passed through the column under the optimal experimental conditions. As shown in Table 4, the values of LODs with NH_2-MCM-41 and NH_2-MCM-48 were 0.056 and 0.045 ppb for Au, and 0.095 and 0.086 ppb for Pd, respectively. These results were obtained according to the equation $C_{LOD} = K_b S_b / m$ [43] for a numerical factor $k_b = 3$.

The precision of the method under the optimum conditions was determined by performing 10 replicates trials. The recoveries were found to be 99.8% ± 0.5 and 99.7% ± 0.7 for Au(III), and 98.7% ± 1 and 99% ± 0.5 for Pd(II) with NH_2-MCM-41 and NH_2-MCM-48, respectively. In order to investigate the accuracy and applicability of this method, real samples and a sample of standard material were analyzed. With these analyses, the effect of different matrices on the

Table 5
Recovery and determination of gold and palladium in various environmental 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	
	Au	Pd	Au	Pd	Au	Pd	Au	Pd	Au	Pd	Au	Pd	Au	Pd	Au	Pd
Distilled water	0.0 ± 0.0	0.0 ± 0.1	0.0 ± 0.0	0.0 ± 0.1	2.0	2.0	2.0	2.0	2.0 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	99.5	98.5	99.5	99.0
Tap water	0.0 ± 0.1	0.1 ± 0.1	0.0 ± 0.1	0.0 ± 0.1	2.0	2.0	2.0	2.0	2.0 ± 0.1	2.1 ± 0.1	2.0 ± 0.1	2.0 ± 0.2	99.0	101.0	98.0	99.0
Wastewater	51.9 ± 0.8	7.2 ± 0.1	52.0 ± 0.1	8.7 ± 0.1	50.0	10.0	50.0	10.0	99.4 ± 0.5	16.2 ± 0.1	100.3 ± 0.6	17.5 ± 0.1	97.5	94.2	98.3	93.8
Soil	12.4 ± 0.6	0.2 ± 0.2	12.3 ± 0.4	0.0 ± 0.1	10.0	2.0	10.0	2.0	22.6 ± 0.4	2.2 ± 0.2	22.3 ± 0.5	2.1 ± 0.1	101.0	99.0	100.0	102.0
Standard material	260.0 ± 0.4	0.0	260.0 ± 0.4	0.0	0.0	0.0	0.0	0.0	265.0 ± 1.0	0.0	264.0 ± 1.0	0.0	101.9	-	101.5	-

proposed method was evaluated. For the sample preparation, certain amounts of Au(III) or Pd(II) were spiked into the solutions and the results of recovery with three replicates are shown in Table 5. In all cases, the gold and palladium recovery was almost quantitative. Somewhat higher levels of gold and palladium recoveries in the soil sample could be attributed to the presence of impurities in the soil.

4. Conclusions

A solid phase extraction procedure based on modified mesoporous silica (NH_2-MCM-41 and NH_2-MCM-48) is very simple, fast, reproducible and selective for the quantization of precious metals. Compared with other solid phases, NH_2-MCM-41 and NH_2-MCM-48 have the advantages of a high capacity factor, a low limit of detection and a high enrichment factor. Due to the relatively high preconcentration factor, trace metal ions at ppb level in high volume economical samples can be determined and separated by functionalized mesoporous silica. The optimum parameters for NH_2-MCM-41 and NH_2-MCM-48 were found to be almost identical with the single point of difference between the optimum conditions being flow rate. Apparently, NH_2-MCM-48, with an interconnected three-dimensional pore network can adsorb metal ions faster than NH_2-MCM-41.

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