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An optimized procedure for preconcentration, determination and on-line recovery of palladium using highly selective diphenyldiketone-monothiosemicarbazone modified silica gel

R.K. Sharma[a,*], Amit Pandey[a], Shikha Gulati[a], Alok Adholeya[b]

[a] Green Chemistry Network Centre, Department of Chemistry, University of Delhi, Delhi- 110007, India
[b] Biotechnology and Management of Bioresources Division, The Energy and Resources Institute, Darbari Seth Block, India Habitat Centre, Lodhi Road, New Delhi- 110003, India

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ABSTRACT

A novel, highly selective, efficient and reusable chelating resin, diphenyldiketone-monothiosemicarbazone modified silica gel, was prepared and applied for the on-line separation and preconcentration of Pd(II) ions in catalytic converter and spiked tap water samples. Several parameters like effect of pH, sample volume, flow rate, type of eluent, and influence of various ionic interferences, etc. were evaluated for effective adsorption of palladium at trace levels. The resin was found to be highly selective for Pd(II) ions in the pH range 4–5 with a very high sorption capacity of 0.73 mmol/g and preconcentration factor of 335. The present environment friendly procedure has also been applied for large-scale extraction by employing the use of newly designed reactor in which on-line separation and preconcentration of Pd can be carried out easily and efficiently in short duration of time.

1. Introduction

Palladium and its alloys have an extensive range of applications in various fields such as dentistry, metallurgy, instrument manufacturing, and chemical industries. The most significant and prevalent application of palladium is in the field of catalysis [1] and automotive catalytic converters [2] which leads to its accumulation in the environment. At the same time, palladium compounds are considered to be highly toxic and carcinogenic, and available evidences indicate that palladium is easily transported to biological material through plant roots, and ultimately intensified along the food chain [3]. The excessive exposure to palladium causes adverse health effects in humans such as primary skin problems, eye irritations, substantial degradation of DNA and cell mitochondria, and aggravation of hydroxyl radical damage and inhibition of the enzymes activity [4]. As the number of ecological and health problems associated with palladium contamination continues to rise, its determination and extraction is becoming very important in order to minimize its hazardous impact on human health and environment. But, in environmental matrices palladium is present at trace levels; therefore, there is a need to develop new sensitive analytical methods incorporating on-line separation and preconcentration steps, which not only make it feasible to detect the metal ions but also separate the analytes from matrix interferences. Several analytical techniques such as coprecipitation, cloud point extraction, solvent extraction, electrodeposition and membrane filtration [5–13] have been employed for separation and preconcentration of Pd(II) ions. But, these techniques suffered from various drawbacks such as lack of sensitivity and selectivity, high cost, and use of large amount of toxic organic solvents which are harmful to human health and environment. Thus, solid phase extraction (SPE) [14–17] has emerged as an excellent separation technique in recent years in comparison to traditional extraction methodologies because of its numerous advantages of high enrichment factor, better separation, high selectivity and efficiency, ease of recovery and reusability, low cost because of lower consumption of reagents, less utilization of organic solvents and more importantly environment friendly. Furthermore, SPE also has the ability of easier integration into an automated analytical technique in on-line mode which has received significant interest during recent years, and is widely applied for selectivity and sensitivity enhancement. Thus, chelating resins, which can be easily prepared by immobilizing a metal specific chelating agent on the support material, are frequently used for preconcentration and separation of metal ions from interfering constituents. Among various support materials, silica gel is an extensively used support for various solid phase extractors because of its numerous advantages like high chemical and thermal stability, ready availability, economic viability, and easy and robust immobilization on its surface [18].

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* Corresponding author. Tel.: +91 011 27666250; fax: +91 011 27666250.
E-mail address: rksharmagreenchem@hotmail.com (R.K. Sharma).

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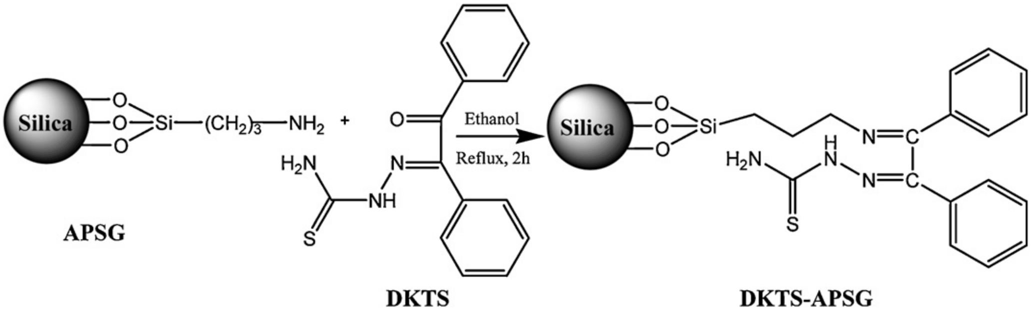


Scheme 1. Preparation of DKTS–APSG resin.

In our ongoing contribution towards development of environment friendly strategy for extraction of metal ions using chelating resins [19–23], herein, we report a novel method for the selective recovery and determination of Pd(II) ions using silica based diphenyldiketone-monothiosemicarbazone chelating resin. Moreover, we have scaled up the procedure for on-line extraction by employing the use of newly designed reactor [24] in which on-line separation and preconcentration of Pd(II) ions can be carried out easily and effectively on large scale in short duration of time.

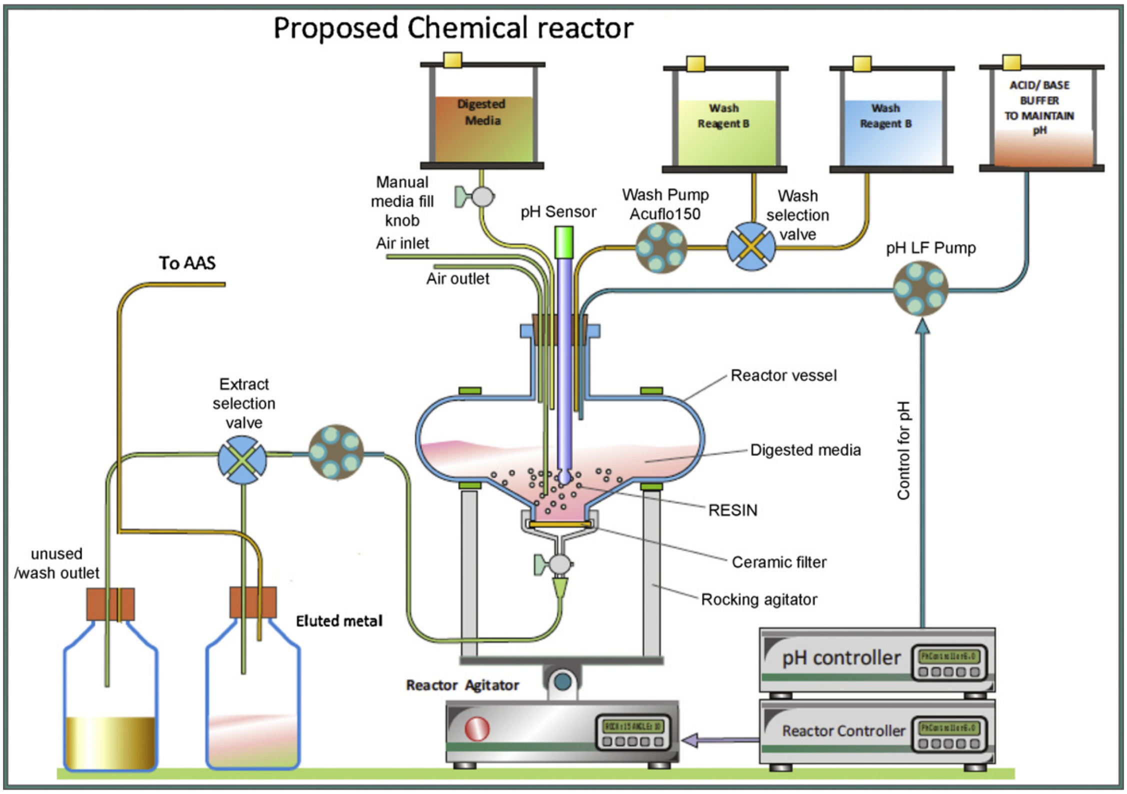
2. Experimental

2.1. Instrumentation

FT-IR spectra were recorded on a Perkin–Elmer spectrometer at room temperature using KBr pellet technique in the range of 4000–400 cm^{-1} under the atmospheric conditions with a resolution of 1 cm^{-1}. The pH measurements were carried out using ELICO LI 120 pH meter. LABINDIA AA 7000 Atomic absorption spectrometer was employed for the determination of metal ion. The optimum parameters for Pd measurements are: wavelength, 244.4 nm; lamp current, 3 mA; slit width, 0.2 nm; fuel flow rate, 1.5 $L\,min^{-1}$, and air flow rate, 1 $L\,min^{-1}$. The SEM images were recorded on ZEISS EVO 40 instrument. The surface area (BET) was measured with Gemini-V2.00 instrument (Micromeritics Instrument Corp.). Thermo gravimetric analysis was performed on DTG-60 Shimadzu instrument equipped with TG units at a heating rate of 10 °C/min from 37 °C to 600 °C in N_2 atmosphere. Quantitative elemental analysis (CHN) was performed using Elementar Analysensysteme GmbhVarioEL.

2.2. Reagents and solutions

All the reagents used were of analytical grade. Silica gel and 3-aminopropyltriethoxy silane (APTES) were procured from Sigma Aldrich (India). Diphenyldiketone and thiosemicarbazide were obtained from Spectrochem Pvt. Ltd. (India). Stock solutions of different metal ions containing 1000 mg/L of metal were used. All working solutions were prepared by stepwise dilution of stock



Scheme 2. Schematic diagram for on-line extraction and preconcentration of metal ions.

Table 1
Physico-chemical parameters of silica gel (SG), aminopropyl silica gel (APSG) and DKTS–APSG resin.

Material	Elemental analysis				Thermal analysis		BET surface area (m^2/g)
	%C	%H	%N	%S	Δm/%[a]	ΔT/°C[b]	
Silica gel	–	–	–	–	–	–	235.67
APSG	6.60	2.38	2.20	–	5.50	0–180	152.04
					2.80	180–600	
DKTS–APSG	14.12	3.39	3.89	2.36	3.80	0–180	83.66
					19.00	180–600	

[a] Change in mass of material.
[b] Change in temperature.

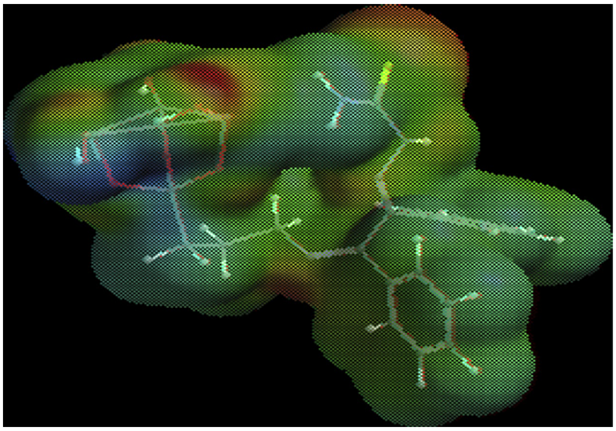


Fig. 1. Electrostatic potential map of the monomeric unit (a perspective view) of DKTS–APSG.

solutions with double-distilled water, and their pH were adjusted using the buffer solutions.

2.3. *Preparation of diphenyldiketone-monothiosemicarbazone (DKTS)*

Diphenyldiketone-monothiosemicarbazone (DKTS) was prepared according to the reported procedure [25]. Equimolar amount of thiosemicarbazide (0.05 mol) and diphenyl diketone (0.05 mol) were dissolved in ethanol (250 ml) and refluxed for 4 h in presence of 2 ml of acetic acid. After the completion of reaction, orange precipitate of the product was filtered and recrystallized from ethanol.

2.4. *Preparation of diphenylketone-monothiosemicarbazone modified silica (DKTS–APSG)*

Aminopropyltriethoxysilane (1 ml) was dissolved in 100 ml of distilled water and acidified with acetic acid (pH 4). Then, 2 g of activated silica was added to the solution and stirred for 2 h at room temperature [26]. The product was filtered off and kept in oven at 150 °C for 4 h. The obtained aminopropyl silica gel (APSG) was washed repeatedly with water, ethanol, and acetone for removal of un-reacted material, and then dried in the oven at 120 °C for 24 h. For immobilization of DKTS on APSG, 5 g of APSG was suspended in 50 ml of ethanol; 2 g of DKTS was then added to suspension and refluxed for 2 h. The orange colored crystalline solid obtained (DKTS–APSG) was filtered, washed with ethanol and dried under vacuum at 110 °C for 4 h (Scheme 1).

2.5. *Sample preparation*

The crushed and ground portion of the catalytic converter sample (0.25 g) was taken in beaker (100 ml) containing 25 ml of aqua-regia and the mixture was evaporated to nearly dryness. The white insoluble part was collected and dissolved in 100 ml water. Finally, the pH of the solution was adjusted to 4 with acetate buffer. For the analysis of tap water samples, water was taken directly from tap and spiked with Pd(II) ions. The resultant water sample was adjusted to required pH using buffer solution.

2.6. *Analytical procedures*

2.6.1. *Column method*

A glass column (15 cm long), having a stopcock and a fritted porous disc (2.5 cm in diameter) was loaded with 50 mg of APSG–DKTS resin. It was washed with double-distilled water and conditioned with the buffer solution (sodium acetate/acetic acid) to the desired pH of 4. After conditioning, sample solution (10 ml) was passed in the column on to the resin bead at a flow rate of 10 ml/min. The adsorbed metal ion was then desorbed using 5 ml of eluting agent (mixture of HCl and thiourea) at a flow rate of 15 ml/min, and subjected to flame atomic absorption spectrometry for metal analysis using the optimum parameters. After every run, the resin in the column was washed with double distilled water and stored for the subsequent run.

2.6.2. *Batch method*

50 mg of APSG–DKTS resin was added to 250 ml glass stoppered bottle containing 10 ml of metal ion solution (5 μg/ml). The solu-

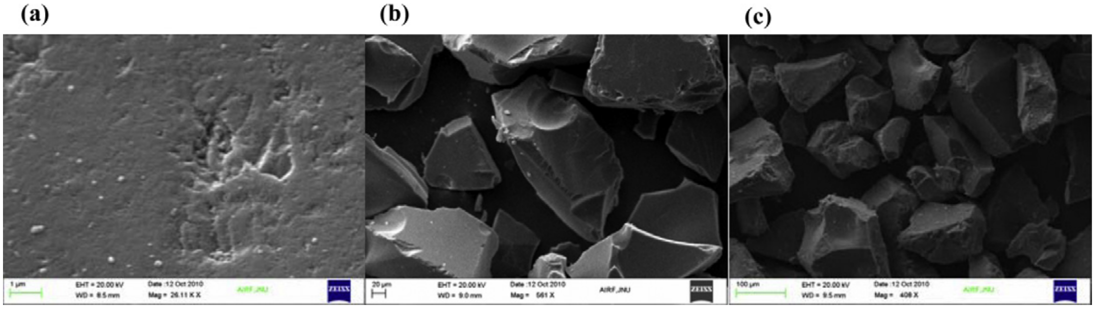


Fig. 2. SEM images of fresh DKTS–APSG chelating resin, (a) at high magnification (26.11K×) (b) at low magnification (561×), and (c) the resin reused for 10 cycles (Magnification 408×).

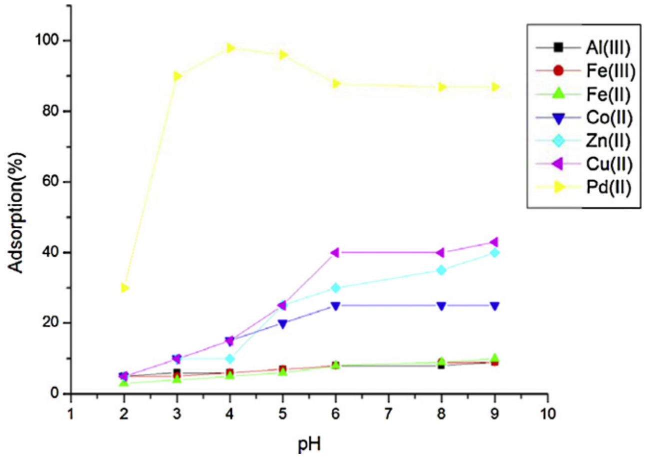


Fig. 3. Effect of pH on adsorption of Al(III), Fe(II), Fe(III), Co(II), Zn(II), Cu(II) and Pd(II) onto DKTS–APSG resin. 50 mg resin, 10 ml test solution.

tion was adjusted to the desired pH of 4 and was kept on shaker for 30 min. The resin was then filtered, and concentration of the metal ion in the filtrate was determined by flame atomic absorption spectrophotometer using the same optimum parameters.

2.6.3. Determination of adsorption capacity

For determination of adsorption capacity, 0.1 g of the resin was shaken with 50 ml of solution containing different concentrations of metal ion (10–500 μg/ml) in batch mode for 2 h at room temp. The filtrate from each flask was then subjected to AAS for the determination of metal ion present after requisite dilution. Adsorption capacity was calculated using the following equation $Q = (C_o - C_e)V/w$, where Q represents adsorption capacity (mg/g), C_o and C_e are the initial and final concentrations of metal ion (mg/l), w is the weight of the resin and V is the volume of metal ion solution.

2.6.4. On-line separation of palladium

The on-line extraction and preconcentration system (Scheme 2) has been designed, which consists of the following units: (i) Batch extractor with a volume capacity of 5–10 L fitted with an agitator, (ii) pH adjusting unit consisting of a pH controller with a probe electrode and buffer solution chambers, and (iii) Elution unit containing suction pump attached to the extractor through polypropylene tube in order to pump out the solution from extractor at a controlled flow rate. Initially, the batch extractor was charged with an optimized amount of silica supported chelating resin (DKTS–APSG), and then the metal ion solution was poured into it through an inlet tube. The pH of the solution was adjusted to required value with the help of pH adjusting unit, and thereafter the mixture in the extractor was subjected to agitation for an appropriate time. After the adsorption of metal ion on the resin, the solution was pumped out through a polypropylene tube at the bottom of the extractor. Then for desorption of metal ion from the resin, selected eluting agent entered through the wash selection valve of the extractor for the elution. The concentration of metal ion was determined directly by aspirating the desorbed metal ion solution into atomic absorption spectrophotometer.

Table 2
Influence of eluting agents on % recovery of the metal ions.

Eluting agent	Volume for maximum recovery (ml)	Recovery (%)
0.1 M HCl	5	40
0.2 M HCl	5	45
1.0 M HCl	6	50
2.0 M HCl	5	60
0.5 M HNO_3	6	42
1.0 M HNO_3	6	50
1.0 M H_2SO_4	6	44
0.1 M thiourea	5	65
0.5 M thiourea	6	75
1 M HCl + 0.1 M thiourea	5	92
2 M HCl + 0.1 M thiourea	5	96
2 M HCl + 0.5 M thiourea	5	98.5

Table 3
Tolerance limit of the foreign ion species in presence of Pd(II) ions (5 μg/ml).

Foreign species	Tolerance limit (g/l)	Recovery (%)
NaCl	2.92	94.4
Na_2SO_4	7.10	93.3
$NaNO_3$	4.20	95.0
Na_3PO_4	4.14	94.0
KCl	3.72	93.5
KI	1.60	98.0
$CaCl_2$	1.10	96.4
$MgCl_2$	4.76	96.7
NH_4Cl	2.67	95.5
Cu^{2+}	0.30	96.4
Cd^{2+}	0.20	92.8
Zn^{2+}	0.50	95.0
Cr^{3+}	0.70	98.0
Co^{2+}	0.70	97.8
Al^{3+}	1.00	98.3
Fe^{2+}	0.25	96.3
Mo^{6+}	1.00	98.6

3. Result and discussion

3.1. Characterizations of APSG-DKTS resin

3.1.1. FT-IR spectroscopy

The grafting of APTES on silica gel and its subsequent functionalization with DKTS has been confirmed by FT-IR spectroscopy (Supplementary information). The peak at 990 cm^{-1} in case of silica gel is assigned to silanol group. But in case of APSG, the peak due to silanol group has disappeared and the peak in the range of 2900–2800 cm^{-1} due to $-CH_2$ groups is observed which confirmed that APTES has been attached to silica gel. In the spectrum of grafted ligand the characteristic band of the imine group (C=N) appears at 1646 cm^{-1}. The spectrum of the adsorbed resin after adsorbing Pd(II) ion shows a peak at 600 cm^{-1} and also the frequency of C=N stretch frequency has been shifted compared to un-adsorbed resin confirming the covalent anchoring of DKTS on APSG.

3.1.2. Elemental and thermal analysis

The quantitative estimation of modified surfaces (APSG and DKTS–APSG) was performed with elemental and thermogravimetric analyses (Table 1). The results of elemental analysis of APSG (nitrogen wt.% = 2.20, carbon wt.% = 6.60 hydrogen wt.% = 2.38) gives rise to the grafting capacity of 1.57 mmol/g, and C/N ratio was found to be ~3 which is close to the expected value thereby confirming the 3-APTES grafting on silica gel. The loading of DKTS on APSG was found to be 0.74 mmol/g of silica using elemental results of APSG–DKTS (nitrogen wt.% = 3.89, carbon wt.% = 14.12 hydrogen wt.% = 3.39, sulfur wt.% = 2.36%). The presence of sulfur in the resin confirmed the grafting of DKTS on APSG. The TGA of the resin exhibited the mass loss of 3.8% in the first degradation assigned to absorbed water on the resin. In the second degradation, a mass loss of 19% was observed due to the decomposition of organic matter between 180 and 600 °C. The calculated loading of DKTS on APSG was found to be 0.74 mmol/g of silica which is in agreement with the results of elemental analysis.

Table 4
Comparison of important analytical characteristics of various support materials used for the separation and preconcentration of Pd(II) ions.

Type of sorbent/ligand	Support material	Adsorption capacity (mmol/g)	Preconcentration factor	LOD (ng/ml)	Ref.
Dithiooxamide	Polystyrene divinylbebzene	0.10 mmol/g	–	-	[27]
Isodiphenylthiourea	Silica gel	0.18 mmol/g	–	4.7	[28]
Thiophene-2-carbaldehyde	Mesoporous silica	5 mg/g	100	0.20	[29]
N-allyl-N-propyl thiourea	Silica gel	0.8 mmol/g	100	0 .05	[30]
Dimethyl glyoxime	Silica gel	4.06 mg/g	75	1200	[31]
Thioridazine·HCl	Octa-decyl silica	–	100	12.0	[32]
Morin	Silica gel	0.24 mmol/g	100	210	[33]
Thiourea	Silica gel	0.29 mmol/g	20	21	[34]
Benzilmonopyridylhydrazone	Silica gel	0.65 mmol/g	250	0.1	[35]
BrPMAA (N-(4-bromophenyl)-2-methacryl amide)/AMPS (acrylamido-2-methyl-1-propane sulfonic acid)	–	–	75	1100	[36]
Thiourea	Melamine formaldehyde	0.14 mmol/g	–	-	[37]
Polyethylineimine	Alumina	13 mg/g	300	0.042	[38]
Modified carbon nanotube	–	15.6 mg/g	165	0.30	[39]
p-Dimethylaminobenzylidene	PEG (Poly ethylene glycol)	0.09 mg/g	125	0.54	[40]
Iminodiacetic acid	Silica gel	0.19 mmol/g	150	800	[41]
Ion imprinted polymer	–	9.25 mg/g	–		[42]
SFODME (solidified floating organic drop micro extraction) based on USD (Ultra sound dispersion)	–	–	49.9	0.6	[43]
1-(2-Pyridylazo)-2-naphthol	Nanoclay	2.4 mg/g	140	0.1	[44]
[1,5-Bis(2-pyridyl)-3 sulphophenyl methylene thiocarbonohydrazide	Dowex1X8-200	–	8.7	2.0	[45]
Phenanthrenequinone-thiosemicarbazone	Silica gel	0.31 mmol/g	–	-	[46]
Diphenyldiketone-monothiosemicarbazone	Silica gel	0.73 mmol/g	335	5.0	Present

3.1.3. BET surface area analysis

The anchoring of organic moieties onto the silica matrix obstructs the access of nitrogen gas molecules, thus reducing its surface area. As a result, as expected, the BET surface area decreased after grafting, according to the sequence SG > APSG > DKTS–APSG. The reduction in surface area in this order confirms the functionalization of silica gel with 3-aminopropyltriethoxy silane to give APSG, and its modification with DKTS to yield a chelating resin. The BET surface area of silica gel (SG), aminopropylsilica gel (APSG) and chelating resin DKTS–APSG were measured and presented in Table 1.

3.1.4. Theoretical studies (molecular modeling)

In order to identify the binding sites on chelating resin (APSG–DKTS), molecular modeling was carried out using Spartan 08 software. The molecular geometry of the resin was optimized by Semi-Empirical (PM 3) method, and its electrostatic potential map (Fig. 1) was generated which provides insight into the nature of molecular recognition in ligand–metal bonding. The better coordinating sites for the metal are the ones which have relatively more negative electrostatic potential surface. Therefore, the available electron rich sites (red region) for binding of metal are N atom of C═N and S atom of C═S functionalities.

3.1.5. Scanning electron microscopy (SEM)

The morphology of the chelating resin was characterized by SEM. SEM image at high magnification (26.11K×) (Fig. 2a) clearly depicts the uniform dispersion of chelating agent on silica. During the preparation of chelating resin, the silica gel beads were subjected to continuous stirring but it is evident from SEM image at low magnification (561×) (Fig. 2b) that silica gel beads remain intact confirming its good mechanical strength. The SEM micrograph of reused (10 cycles) resin is also obtained (Fig. 2c) which confirms the stability of the prepared resin for its reusability even after several cycles.

3.2. Extraction studies

3.2.1. Effect of pH

The effect of pH was found to be the most critical parameter for the adsorption of metal ions. The influence of pH on the adsorption of Al(III), Cr(III), Fe(III), Co(II), Fe(II), Zn(II), Pd(II), Cu(II) was investigated in the pH range of 2–9. Experimentation was carried out by passing 10 ml of test solution containing 5 μg/ml of each analyte at different pH values. The percentage adsorption of different metal ions is shown in Fig. 3, and it was found that the resin showed maximum adsorption for Pd(II) ion in the pH range of 4–5. Hence, further studies were carried out for Pd(II) ion at pH 4.

3.2.2. Selection of eluting agent

In order to investigate the most efficient eluting agent, first 10 ml of 5 μg/ml Pd(II) ion solution was adsorbed on the resin and then eluted with varying concentration of HNO_3, HCl, H_2SO_4 and thiourea using different volumes (1–6 ml). Among these eluting agents, mixture of HCl and thiourea (5 ml) gave maximum recovery and hence selected as an appropriate eluting agent for further applications. The results are shown in Table 2.

3.2.3. Reusability of the column

To ensure the stability and reusability of the resin, palladium was sorbed and desorbed on the resin in ten successive cycles. The column was reused after regeneration with 10 ml of mixture of thiourea (0.5 M) and HCl (2 M) and 100 ml distilled water, respectively, followed by vacuum drying. The adsorption capacity of the resin was found to be apparently constant even after its repeated use for 10 cycles. The surface morphology of the recycled resin was monitored with the help of scanning electron microscopy (SEM). The SEM micrograph of reused resin (10 cycles) shows the same morphology (Fig. 2c) as that of fresh resin (Fig. 2b) confirming its high mechanical stability. Thus, its high stability and reusability makes the present protocol environmentally benign.

3.2.4. *Effect of flow rate of metal ion solution and eluting agent*

The flow rate of sample solution and eluting agent through the column is an imperative parameter for controlling the time of adsorption and analysis. The influence of flow rates were investigated in the range of 2–15 ml/min for Pd(II) ion solution, and it was observed that variable sample flow rate (rate at which sample solution is poured into the column) had no effect on the adsorption of metal ion up to 10 ml/min. At higher sample flow rates (>10 ml/min) the adsorption of metal ion was decreased by 20% (as increase in the flow rate allows less time for equilibration of metal ion with resin). Also, the eluent flow rate (rate at which the sample solution moves out of the column) had no effect up to 15 ml/min. Therefore, 10 ml/min was selected as sample flow rate and 15 ml/min was selected as flow rate for elution for further studies.

3.2.5. *Effect of sample volume and preconcentration factor*

To enrich the low concentration of analytes from the large sample volume, preconcentration factor and effect of sample volume were determined. The effect of sample volume was studied by passing 250–2500 ml of metal solution through the column (fed with 0.1 g of resin) and keeping the total amount of loaded metal ion constant at 10 ng/ml and 20 ng/ml. The adsorbed metal ion was recovered by optimized eluting agent. The adsorption of metal ion was not affected by sample volume till 2000 ml. In the present work, the preconcentration factor was found to be 335 for 2000 ml of sample volume eluted with 6 ml of eluting agent.

3.2.6. *Adsorption isotherm*

To examine the adsorption behavior of resin, solution of metal ion in the range of 10–500 μg/ml were taken in the batches containing 0.1 g of chelating resin at room temperature. The concentration of un-adsorbed metal ion was determined by AAS. Langmuir equation, $C_e/Q = 1/Qb + C_e/Q_m$ was applied to determine the adsorption capacity of resin, where C_e is equilibrium concentration of metal ion, Q is the amount of metal ion adsorbed at equilibrium, Q_m is the maximum amount of adsorbed metal ion (76.92 mg/g), and b is the binding constant (0.26 L/mg). The amount of total metal sorbed on 1.0 g of resin is calculated from the plot obtained (Fig. 4).

3.2.7. *Effect of interfering ions*

In order to examine the selectivity of the prepared resin for the determination and preconcentration of Pd(II) ions, effect of various electrolytes and metal ions were studied by varying the concentrations of added electrolytes from (1 to 10 g/L) in 10 ml solution of Pd(II) ions (5 μg/ml). The effect of coexisting metal ions on the adsorption of Pd(II) ion was studied in binary mixtures as well as in multi-component mixture and no interference was observed up to the considerable concentration (100 μg/ml). The tolerance limit (defined as the ion concentration causing a relative error of not more than 5%) of investigated electrolytes are given in Table 3, and found that many cations and anions, which are inevitably associated with Pd(II) ions at trace levels, produce no interference in the adsorption of Pd(II) ions up to an appreciable concentration.

3.2.8. *Analytical performance (accuracy, precision and limit of detection)*

The validity, accuracy and precision of the proposed method were tested by spiking known amount of metal ion, and it was found that the added and measured amount of analyte are in agreement with each other signifying the accuracy. The precision of the method under the optimum conditions was determined by performing 5 replica trials. The recoveries were found to be (>98%) with low relative standard deviation values (<2%). The obtained results (shown in Table 4) thus authenticate the accuracy and precision of the present procedure, and its interdependence from the matrix effect. For ten replicate measurements, LOD (Limit of detection, the amount of palladium required to give net signal equal to three times the standard deviation of signal for blank solution) was determined by passing 100 ml of solution through the column loaded with resin and fount to be 5 ng/ml. The equation of the calibration curve is $Y = 0.0146X + 0.0061$ with correlation coefficient of 0.9982, where Y is the absorbance and X is the concentration of the Pd(II) in μg mL^{-1}.

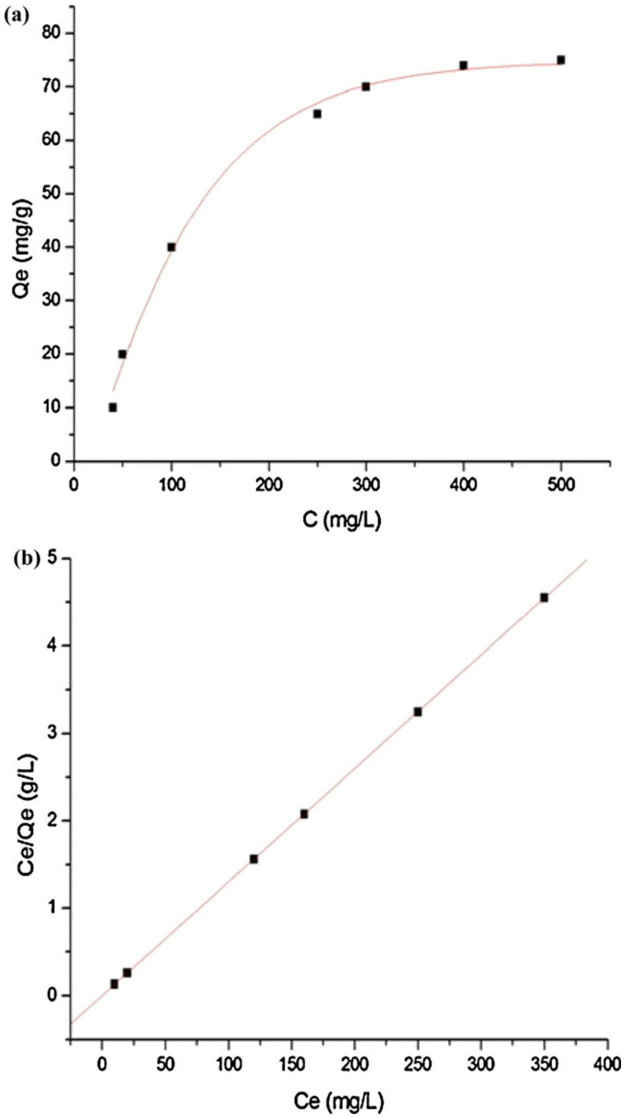


Fig. 4. (a) Adsorption isotherm of Pd(II) ions onto DKTS–APSG and (b) the linear form of the Langmuir adsorption isotherm. 100 mg resin, 50 ml test solution, pH 4.

3.2.9. *On-line separation*

We have also performed the mentioned procedure for on-line separation and preconcentration of Pd(II) ions at bulk scale using newly designed reactor. On the basis of the aforementioned optimized conditions, 5 g of the resin was taken in the reactor and applied for online separation of palladium from the 2 L of metal ion solution (250 μg/ml) with the help of the route elaborated in Section 2.6.4. The adsorption capacity was found in good agreement with the earlier determined value using column method on smaller scale. After the recovery of Pd(II) ions, the resin was washed, dried and recycled for next run.

Table 5
Analytical results for Pd (II) ions in tap water and catalytic converter samples.

Sample	Concentration of palladium (μg)		
	Added	Found (RSD)	Recovery (%)
Tap water	12.5	12.10 (1.25)	96.80
	25.0	24.65 (1.10)	98.60
Catalytic converter	–	33.12 (1.5) (without using resin)	–
Catalytic converter	–	30.11 (1.20) (using resin)	98.05
	25.0	54.05 (1.15)	98.07
	40.0	69.50 (1.10)	99.10

3.2.10. Comparison of the prepared resin with the literature precedents

Table 5 represents the literature precedents [27–46] of various sorbents for extraction of Pd(II) ions, and their analytical results have been compared with those obtained by using DKTS–APSG chelating resin. It is evident from the comparison of the results obtained that adsorption capacity and preconcentration factor of the present resin is very high making it superior to the reported ones in terms of selectivity, sensitivity and reusability [47].

4. Applications of the proposed method

4.1. Determination of Pd(II) ions in spiked tap water samples

For the preconcentration procedure, pH of water sample was adjusted to 4 and spiked with Pd(II) ions, and then subjected to the DKTS–APSG chelating resin. The sorbed Pd(II) ions were estimated using atomic absorption spectrometer. It was found that the resin was successful in quantitative extraction of the Pd(II) ions even in the presence of miscellaneous ions (Table 5).

4.2. Determination of Pd(II) ions in catalytic converter sample

The applicability of the DKTS–APSG resin for the preconcentration of Pd(II) ions at trace level of was also tested using the catalytic converter sample. After the digestion of catalytic converter sample, the solution was adjusted to pH 4 and subjected to the DKTS–APSG chelating resin. The results are shown in Table 5.

5. Conclusion

We have developed an easy, efficient and environmental friendly methodology for the on-line determination of Pd(II) ions using a novel solid phase extractor, diphenyldiketone-monothiosemicarbazone functionalized silica gel. The proposed solid-phase extraction system for the first time enables an effective on-line palladium preconcentration and final determination of trace amount of Pd(II) ions in various samples with complex and variable matrices as a result of its excellent analytical characteristics such as low detection limit (5 ng/ml), high enrichment factor (335), high adsorption capacity (0.73 mmol/g) and good selectivity and precision. By using on-line solid phase extraction system, a large volume of samples (environmental/waste effluents) can be injected, and resin could continuously be used for a long period of time without any appreciable change in its sorption properties towards Pd(II) ions. Therefore, this is not only a practicable method for palladium trace analysis in a variety of matrices in order to reduce its hazardous impact on ecosystem but also a value addition because of the recovery of costly palladium metal.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.01.022.

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