Metal Ion Extraction with Imino Diacetic Acid Immobilised Silica Gel

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ABSTRACT: The sorption of Pd (II) on iminodiacetic acid (IDA) anchored silica gel was studied. The optimum pH range for quantitative sorption is 4.5-5.5. The sorption of Pd follows the Langmuir Model. It is useful to analyze Pd in synthetic material. The Padladium content of synthetic solutions cooresponding to standard reference materials was analyzed.

Keywords: Silica gel; Iminodicatic acid; Column method and Batch method.

INTRODUCTION: The ligands of diverse types have been immobilized on the silica gel surface & resulting matrices explored for metal extraction formylsalicyclic acid has been immobilized on silica gel using aminopropyltriethoxysilane and is used for extraction of Fe (III). In Designing chelating matrices of high sorption capacity and pre concentration factor it is worthwhile to explore immobilization of sterically less demanding ligands on silica gel which has high surface. IDA having oxygen donor sites to ligate with hard metals are good legand candidates for such designing and have been immobilized on the silica gel surface and explore for metal extraction. The IDA modified silica gel is standardized for enrichment of Pd (II) and applied to standard reference materials (SRM). The results of these investigations are the subject. The matrix can sorb metal ion via chelation through C-N and two carboxylic groups
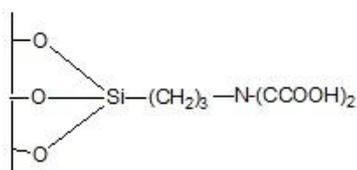

Figure 1: Segment of IDA Immobilized Silica Gel.

MATERIALS AND METHODS: The column and batch methods both were optimized for sorption and subsequent elution of Pd(II) on IDA immobilized silica gel. A flame atomic absorption spectrometer standardized at appropriate wavelengths (Table 1) is used for the determination of metal ions.

The following conditions for the sorption and desorption for each metal ion were established by varying parameter and keeping the constant at optimum level.

- PH range
- Flow rate
- Acid concentration for elution
- Elution breakthrough volume
- Average recovery

The recommended column and batch methods based on the optimized acreters are follows:

Recommended procedure for pre-concentration and Determination of Metal Ions:

Column Method: The glass column was packed with 1.0 g of iminodiacetic acid (IDA) immobilized silica gel iminiacetic acid (IDA) immobilized silica gel was treated with HNO_3 (50ml) and washed with distilled water to remove acid.The column was treated with 2 M HCl or HNO_3 (50 ml) and washed with doubly distilled water until free from acid. A suitable aliquot of the sample solution containing Pd (II) in the concentration range 0.001-1.0 μg ml⁻ was passed the column after adjusting its PH (Table 2) at a flow rate of 1-4 ml min⁻¹,controlled with a peristaltic pump. The column was washed with distilled water to remove free metal ions. The bound metal ions were stripped from the column with 0.1 M HCl containing 3.0% thiourea (10-15 ml). The concentration of the metal ion in the eluate was determined by flame atomic

absorption spectrometry (FAAS), standardized previously.

Batch Method: A sample solution (50 ml) containing 0.20-20.43 μml^{-1} Pd(II) was placed a glass stoppered bottel bottle (250 ml) after adjusting its pH to the optimum value. The DHA loaded silica gel (0.5 g) was added. Sample was shaken for 30 minute and the modify silica gel was shaken with 20-25 ml of 0.1 M HCl containing 30% thiourea for 30 min and then filtered. The filtrate was aspirated through FAAS after dilution.

Table 1: Various Parameters for FAAS Measurements.

Meal ions	ECIL 4129			A Analyst 100		
	Wavelength (A^o)	Slit (nm)	HC lamp current (mA)	Wavelength (A^o)	Slit (nm)	HC lamp current (mA)
Zn(II	213.9	1.0	5.0	213.9	0.7	15.0
Mn(II)	279.5	0.2	5.0	279.8	0.2	30.0
Ni(II)	232.0	0.5	3.5	231.1	0.2	30.0
Pb(II)	217.0	1.0	7.0	217.0	0.7	10.0
Cd(II)	228.8	0.5	3.5	228.8	0.7	4.0
Cu(II)	324.8	0.5	3.5	324.8	0.7	30.0
Fe(III)	248.3	0.5	5.0	248.8	0.2	30.0
Pd(II)	244.8	0.2	30.0	244.8	0.2	30.0
Co(II)	240.7	0.5	7.0	240.7	0.2	30.00

Using the above–mentioned recommended procedures, IDA immobilized silica gel has been evaluated for the following characteristics: Kinetics of metal and effect of electrolytes and stability of the matrix.

RESULTS AND DISCUSSION:

Effect of pH: The effect of pH was studied by taking a set of sample solutions (100 ml) each containing 50 μg of Pd (II). The pH of the solutions of the set was adjusted between 2.0-9.0 using 0.01M HCl, NaOH, acetate, phosphate or NH_3-NH_4Cl buffer. The solutions were passed through the columns containing IDA modified silica gel at a flow rate of 1.0-4.0 ml min^{-1} controlled with a peristaltic pump. The metal ions from the columns were desorbed with 10-25 ml of o.1M HCl containing 3% thiourea passed at a flow rate between 2.0- 5.0 ml min^{-1}. The eluates were aspirated into flame of AAS (previously standardized for each metal at appropriate wavelength to monitor palladium concentration. The recovery was 99.2%. The recovery as a function of pH is shown in Figure 2 and optimum pH range of is given in Table 2.

Effect of flow Rate: A set of solution (100ml each) containing 10-25 μg of Pd(II) ions was taken. The pH of solution of the set was adjusted to an optimum level as given in Table 2. These solution were passed though the column packed with IDA loaded silica gel at varying flow rate (1-25ml min^{-1}) subsequently the loaded metal ions were stripped off the matrix using 10ml of 0.1 M HCl containing 3% thiourea and subjected to FAAS determination. For maximum recovery (99.2%), a flow rate of 1.0 to 4.0ml min was found suitable. The sorption (%) as a function of flow rate is shown in Figure 2.

Table 2: Optimum experimental conditions for the sorption and desorption of metal ion (SG-IDA).

Experimental parameters	Metal ion Pd (II)
pH range	4.0-5.5
Flow rate (ml min)	1.0-4.0/2.5-5.0
Concentration for Desorption (M)	0.1 M**
Sorption capacity (umol g)	192
t1\2(min)	5
Limit of detection (LOD)	0.8
Limit of quantification (LOQ)	1.55
Average recovery (%)	99.2
SD	0.027
RSD(%)	2.32

For five determination
**HCl containing 3% TU
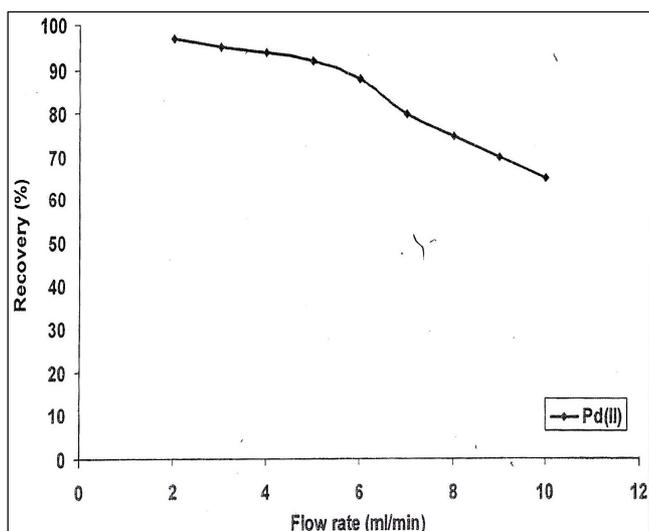
Figure 2: Effect of flow rate on the sorption of the metal ion on SG-IDA.

Figure 3: Kinetics of metal ion sorption on IDA loaded silica gel.

Acid Concentration for Desorption: Palladium soilution (100ml) containing 10-25 μg of the metal was taken and their pH was adjusted to optimum level (Table 1). These solution were passed through the columns of IDA modified silica gel at an optimum flow rate (Table 1). To study the effect of concentration of the acid solution used as eluent on the desorption of metal ions from the IDA modified silica gel column , the metal ion were stripped off from the column with 10 ml of HCl (containing 3% thiourea) of varying concentrations (0.001-0.5 M) keeping optimum flow rate . It was found that 0.1M HCl containing 3% thiourea was sufficient for the quantitative desorption (recovery ~ 98.7%) of Pd.

Breakthrough Volume for Elution: The palladium (II) from solution (100 ml, concentration 0.5μg ml) were loaded on the IDA modified silica gel as described earlier in the recommended column procedure. They were desorbed with varying volumes (1-25 ml) of 0.1M HCl containing 3% TU. It was found that 10ml was sufficient for quantitative recovery (98.7%).

Kinetics of metal Sorption: The kinetics of sorption was studied by batch method. IDA-immobilized silica gel (0.05g) was shaken with 50ml solution containing 40μg ml Pd metal ion for different equilibration times (2,5,10,15,20,25,30,35,40 min and 5h) under optimum condition. The concentration of metal onto the matrix and supertant solution was determined through FAAS after dilution. The variation of sorption for all the medal ions as a function of time is shown in Figure 3. Shaking for 5 min was found to be sufficient for more than 50% sorption of Pd. This indicates that the chelating sites of the present matrix have good accessibility.
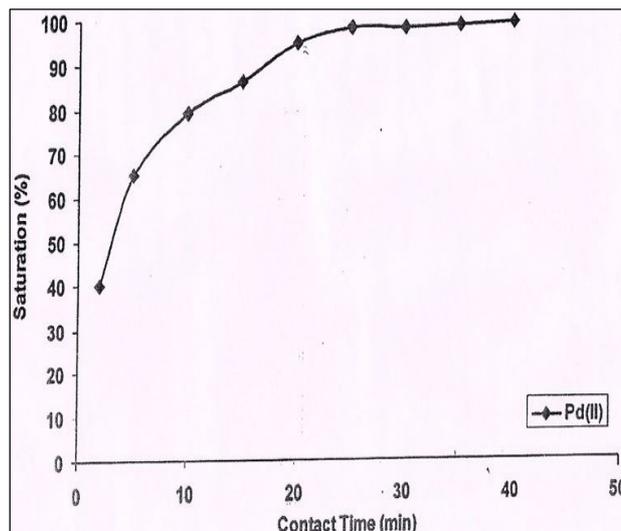
Sorption Capacity: The sorption capacity of each metalion was determined through batch method. A solution (50ml) containing 50 μg ml^{-1} of Pd(II) was placed in a glass stoppered bottle (250ml) after adjusting the pH to the optimum value (Table 1). IDA-loaded silica gel (0.05g) was added to it, and the bottle was stoppered and shaken for 1 h. The solid matrix was filtered and washed with distilled water. It's loaded metal ions were desorbed with 50 ml of 0.1M HCl. Containing 3% TU and determines with FAAS to calculate the capacity. After filtering the matrix the filtrate was diluted and subjected by FAAS to determine the capacity. The capacity value (Table 1) determined by batch and column methods are consistent.

Adsorption Isotherms and Feasibility of the Sorption Process: The ability of the IDA-functionalzied silica gel matrix to sorb cations was evaluated by measuring the sorption isotherms. A series of samples of 0.05g of functionlized silica gel was suspended in 50 ml of aqueous metal ion solutions of different concentrations varying from 5 to 40 mg l^{-1}, and the recommended batch procedure was followed For the series of isotherms obtained analysis of the data revealed that the sorption process conformed to the Langmuir model (Eq.1), Which assumes uniform distribution of sorption sites and sorption energies without interactions between the sorbed species, C_s is the concentration of solution at equilibrium (mg l^{-1}) N_f is the concentration of cations (in mg g^{-1}) sorbed per gram of the matrix. The sorption cofficient N_s is the maximum amount of solute (in mg g^{-1}) sorbed per gram of surface corresponding to a condition in which all available sites are filled.

$$C_s/N_f = C_s/N_s + 1/N_sB \text{ --------------------------(1)}$$

The coefficient b is related primarily to the net enthalpy of sorption. The plots of C_s/N_f against C_s gives the values of N_s are given Table 6B.2. The equilibrium constant (K_c) was calculated from Eq. (2), where C_{AC} is the equilibrium concentration of metal ion sorbed (mg l^{-1}).

$$KC = C_{AC}/C_s \text{--(2)}$$

It was subsequently used for the evaluation of Triangle G of the pocess following the relation.

$$\Delta G = -RT 1nK_c \text{-------------------------------------(3)}$$

Where R (JK^{-1} mol^{-1}) is the universal gas constant and T (K) is the absolute temperature. The value of ΔG suggests the process to be spontaneous and favorable thermodynamically.

Table 3: Thermodyanatic Parameters at 298K.

Metal ion	Parameters: Langmuir Isotherm					
	K_c	$-\Delta G$ (KJ mol^{-1})	N_s (mg g^{-1})	b (1mg^{-1})	R^2	Sorption capacity (mg g^{-1})
Pd (II)	1.58	0.69	11.35	0.33	0.9785	10.68

Effects of Electrolytes and cations: The chloride, nitrate, sulphate and phosphate anions, constituent of natural water samples have the capability to complex with many metal ion. Thus, the effects of NaCl, NaBr, NaNO$_3$, Na$_2$SO$_4$, Na$_3$PO$_4$, NaI and other foreign species on the efficiency of sorption of Pd(II) (25 µg each) on SG-DHB were studies using the recommended column method under the optimum conditions given in table 6B.3. A species is considered to interface when it lowers the recovery of metal on tolerance/Interference is in the pre-concentration and not in the determination by AAS, as checked with the help of reagent matched standard solutions. The tolerance limits of various foreign species in the sorption of Pd metal ion are given in Table 4.

Stability of the Matrix: The IDA modified silica gel was shaken with HCl/HNO$_3$ solutions of varying concentrations (1.0 to 6.0 M) for 4 h and filtered. The solid was washed with distilled water until free of acid and dried at 350 K under vacuum. The sorption capacity determined by the batch method of the acid-treated matrix was found to be similar (< 1.2% variation) to that of the untreated one. Thus, the present resin can withstand HCl or HNO$_3$ of concentration of the order 7.0 at higher acid concentrations it showed signs of degradation and the sorption capacity decreased drastically.

Table 4: Tolerance limit of electrolytes, Ca (II), Mg (II) and organic species with SG-IDA.

Species	Tolerance limits (M/ ^{A} µg ml^{-1}/^{b}n mM) with
NaNO$_3$	0.45
NaCl	0.67
NaBr	0.22
Na$_3$PO$_4$	0.18
Na$_2$SO$_4$	0.58
NaI	0.12
Humic acid[a]	15
Ascorbic acid[b]	0.65
Citric acid[b]	0.25
EDTA[b]	0.014
Tartaric acid[b]	0.75
Ca (II)	0.24
Mg (II)	0.3

Reusability of the Matrix: The Cheating matrix (0.2 g) was shaken on a mechanical shaker with 400ml of solution containing. Pd (20 mgl^{-1}) for 2 h at room temperature under optimum conditions. The bound metal ion were desorbed using 50 ml of 0.1M HCl containing 3% TU by equilibrating the metal ion loaded matrix for 30 min with acid. These loading and elution cycles were repeated on the same sample of matrix. The chelating matrix can be reused forty five times without any significant change (0.8%) in the sorption capacity. The capacity of the resin does not change either when storing it for 12 months in ambient conditions.

Pre-concentration and Recovery of Metal Icons: The column technique is a common procedure for extraction and separation of metal ion from large sample volumes. The ability of the IDA modified silica gel to per-concentrate was determined using the recommended procedure while increasing the dilution of palladium ion solution (15 µg) Total metal. The feed volumes for loading and pre-concentration factor are given in Table 5. The recoveries of the palladium were non-quantitative when its concentrations were below the lowest concentration limit. For Pd(II) ion in the 10 ng ml^{-1}.

Table 5: Enrichment factors and enrichment limits of metal ion (SG-IDA).

Metal	Total Volume (ml)	Concentration (ng ml^{-1})	Final vlume ml)	Recovery %	Preconcentration factor
Pd(II)	1500	10	10	98.7	150

Limit of Detection and quantification: The limit detection and quantification for Pd(II) were determined by passing 5.1 of blank solution through a column loaded with IDA modified silica gel and monitoring the Pd after desorbing it with 0.1 M HCl containing 3% TU with FAAS. The limit of detection (LED) value (defined as blank + 3S Where S is standard deviation of blank determination) and limit of quantification (blank + 10S) are 0.80 and 1.55 µg 1^{-1} respectively.

Application of the method:

Analysis of palladium in synthetic materials: To check the validity and accuracy of the present matrices coupled with FAAS for metal ion monitoring, the recommended procedure was applied to determine palladium content in synthetic solutions (1000ml) corresponding to GBWO7293 geological standard reference material and (Institute of Geophysical and Geochemical prospecting, Langfang, China) auto catalyst NIST SRM 2557 (National Institute of Standards and Technology, Gaither burg, USA). The average of four determinations of palladium was found to be in GBWO7293 44.6 ng g^{-1} (RSD 4.9%). The reported value of palladium in the GBWO7293 IS 45 ng $^{g-1}$. The palladium in the NIST SRM 2557 was found to be 232.6 µg g^{-1} (RSD 6.5%). The amount (µg g^{-1}) of palladium present in NIST SRM 2557 is 233.2 µg g^{-1}.

CONCLUSION: The sorption of Pd(II) on IDS anchored silica gel was studies. The optimum pH range for quantitative sorption is 4.5-5.5. The Pd from the resign can be desorbed with 0.4M HCL Containing 3.0 % thiourea. A flow rate of 1.0-4.0 ml min^{-1} was found suitable for sorption wheres for desorption 2.0-5.0 ml min-1 flow rate was optimum. The sorption capacity of the chealating matrix is 192 µmol^{g-1}. during its sorption without any adverse effect are reported. The t1/2 value is 5 min. Sorption of Pd follows the langmuir mode. The break through volume was found to be 10 ml of 0.1 M HCL Containing 3.0% thiourea (recovery 98.7%). The limit of detection is 0.80 µg1^{-1} and the limit of quantification is 1.55 µg1^{-1}. The pre-concentration factor is 150. The palladium contents of synthetic solutions corresponding to standard reference materials GBWO7293 and NIST SRM 2557 were analyzed.

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