



Separation Science and Technology

ISSN: 0149-6395 (Print) 1520-5754 (Online) Journal homepage: https://www.tandfonline.com/loi/lsst20

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To cite this article: Omolola E. Fayemi, Adeniyi S. Ogunlaja, Edith Antunes, Tebello Nyokong & Zenixole R. Tshentu (2015) The Development of Palladium(II)-Specific Amine-Functionalized Silica-Based Microparticles: Adsorption and Column Separation Studies, Separation Science and Technology, 50:10, 1497-1506, DOI: 10.1080/01496395.2014.978017

To link to this article: https://doi.org/10.1080/01496395.2014.978017



Published online: 04 Jun 2015.

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The Development of Palladium(II)-Specific Amine-Functionalized Silica-Based Microparticles: Adsorption and Column Separation Studies

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The adsorption and separation of platinum(IV) and palladium(II) chlorido species ($[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$) on silica-based microparticles functionalized with ammonium centers based on ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetriamine (TETA) and tris-(2-aminoethyl)amine (TAEA) were investigated. The functionalized sorbent materials were characterized using SEM, XPS, BET, and FTIR. The sorbents were used in the batch and column study for adsorption and selective separation of $[PtCl_6^{2-}$ and $PdCl_4]^{2-}$. The adsorption model for both $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$ on the different sorbent materials fitted the Freundlich isotherm with R^2 values > 0.99. The S-TETA sorbent material was palladium(II) specific. Pd(II) loaded on the silica column was recovered using 3% m/v thiourea solution as the eluting agent. Separation of platinum and palladium was achieved by selective stripping of [PtCl₆]²⁻ with 0.5 M of NaClO₄ in 1.0 M HCl while Pd(II) was eluted with 0.5 M thiourea in 1.0 M HCl. The separation of palladium (Pd) from a mixture containing platinum (Pt), iridium (Ir), and rhodium (Rh) was successful on silica functionalized with triethylenetriamine (TETA) showing specificity for palladium(II) and a loading capacity of 0.27 mg/g. S-TETA showed potential for use in the recovery of palladium from platinum group metals such as from solutions of worn out automobile emission control catalytic convertors and other secondary sources.

Keywords amine functionalized silica; separation; platinum group metals; palladium(II)-specific

INTRODUCTION

Platinum group metals (PGMs) are essential metal elements used in various applications such as catalysts used for automobile emission control, fuel processes, and fuel cells (1–3).

This leads to a quest for efficient processes for their recovery from ore solutions and from secondary sources through recycling. There has been widespread application of modified silica gel with functional chemistries in several solid phase supported systems such as in catalysis (4, 5), ion-exchange (6), chromatography (7, 8), solid phase extraction, and metal ion preconcentration (9, 10). The attraction was due to its good mechanical strength, swelling stability, and fast metal exchange kinetics required for its use in different types of chromatographic systems.

Ion exchangers with (poly)amine groups and silica-based skeleton have been fabricated and applied to the separation of platinum group metals (PGMs) (11). The sorption experiments of Pd, Pt, and Rh ions from the industrial base metal refinery (BMR) effluents and precious metal refinery (PRM) with silica-based (poly)amine ion exchangers exhibited very high selectivity for platinum group metals (PGMs) (11). There was no detectable amount of the other transition metals (Ni, Cu, and Fe). The fact that the ion exchangers originate from relatively inexpensive starting materials and maximum sorption is obtained at room temperature makes the application in a continuous system commercially feasible (12).

The selectivity of the surface with the immobilized functional groups towards metal ion(s) depends on factors like the size of the modifier (12) and the activity of the loaded group (13, 14). Among the different adsorbents, silica gel functionalized with various organic compounds with metal chelating ability has received great attention and the active silica surface with large specific surface area is of great importance in adsorption and ion exchange (15). A silica surface interacts with the silane reagent to form a covalent bond with a silanol group (16). By the introduction of organic functional groups to a silica surface there is a partial conversion of surface silanol to a new organofunctional surface that acquires organophilic properties. Thus, ligand-functionalized silica gives a set of properties to the surface, which differs considerably from the original matrix (17, 18).

Received 8 April 2014; accepted 14 October 2014.

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FIG. 1. Structures of amines used for functionalization (a) EDA (b) DETA (c) TETA (d) TAEA.

The purpose of this work was to functionalize silica microparticles with ammonium centers derived from ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetriamine (TETA), and *tris*-(2-aminoethyl) amine (TAEA) (Fig. 1). Selective separation of platinum and palladium was investigated as well as the separation of palladium from a mixture containing platinum, rhodium and iridium on a TETAfunctionalized sorbent material which showed specificity for palladium(II).

EXPERIMENTAL Materials

3-Chloropropyltrimethoxysilane (97%, Sigma-Aldrich), ethylenediamine (75-80%, Sigma-Aldrich), diethylenetriamine (99%, Sigma-Aldrich), triethylenetetramine (97%, Sigma-Aldrich), *tris*-(2-aminoethyl)amine, (96%, Sigma-Aldrich), *N*,*N*-dimethylformamide (DMF) (99%, Merck Chemical), and sodium iodide (99%, Saarchem chemical) were used as received for the synthesis of the sorbent materials. All other chemicals and solvents were of analytical grade and were used as received.

Instrumentation

The FTIR spectra were recorded on the Perkin Elmer 400 Fourier Transform Infrared (FTIR) and 100 Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectrometers. Elemental analysis was carried out with a Vario Elementary ELIII Microcube CHNS analyzer to determine the nitrogen percentage in the synthesized sorbents. The surface morphologies of the sorbents were observed using a TESCAN Vega TS 5136LM scanning electron microscope (SEM). Carbon dioxide adsorption isotherms on the sorbents were measured at 273 K using a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. X-ray Photoelectron Spectroscopy (XPS) measurements on the unfunctionalized and functionalized sorbents were performed with a Kratos Axis Ultra X-ray Photoelectron spectrometer equipped with a monochromatic Al K_{α} source (1486.6 eV). The analyses of metal ions were carried out with a Thermo Electron (iCAP 6000 Series) inductively coupled plasma (ICP) spectrometer equipped with an optical emission spectrometer (OES) detector.

Synthesis of Silica-Based Microparticles

The respective amine (0.22 mol) was reacted with 3chloropropyltrimethoxysilane (0.2 mol) in 30 mL of dry DMF. Sodium iodide was then added to the mixture, which was then heated under reflux for 6 days (Scheme 1). The product was reacted with 4 g of silica gel for an additional 8 days. The reaction mixture was heated under reflux overnight. The resin was washed with DMF, Soxhlet extracted in methanol, air dried, and sieved if necessary. The same procedure was used for functionalization with the other amines. FT-IR (cm⁻¹): 1046 cm⁻¹ ν (Si-O), 1671 δ (N-H), 3200-3300 ν (N-H). Elemental analysis (C, H, N): Anal. found for; S-EDA (6.49, 1.78, 1.53)%, S-DETA (12.71, 3.35, 4.28)%, S-TETA (12.04, 3.00, 4.31)%, and S-TAEA (4.60, 1.13, 1.76)%.



SCHEME 1. Functionalization of silica-based sorbent with ethylenediamine S-EDA.

Preparation of Metal Solutions

Aqueous solutions of $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$ (0.01 M) were prepared by dissolving 0.3 and 0.2 g of K₂PdCl₄ and K₂PtCl₄ in 1 M HCl, respectively. 20 mL of 10% H₂O₂ solution was added to the latter and the mixture was heated at 50°C for 30 minutes. The binary solution was prepared similarly but just adding the metal salts in the same solution. A mixture of 0.2 g, 0.02 g, and 0.01 g of K₂PtCl₄, RhCl₃, and IrCl₃ xH₂O, respectively, was prepared by the same procedure as above. The species $[PtCl_6]^{2-}$ was confirmed by using ¹⁹⁵Pt NMR spectroscopy (19, 20).

Metal Ion Analysis

Metal ion analyses were carried out with a Thermo Electron (iCAP 6000 Series) inductively coupled plasma (ICP) spectrometer equipped with an OES detector. The platinum and palladium standards were prepared in 1 M HCl for the construction of calibration curves using distilled, deionized, milliQ water for the dilutions. The elements were analyzed at the following US-EPA (21) specified wavelengths (nm) for minimal interferences; 342.1 (Pd²⁺), 214.4 (Pt⁴⁺), 343.4 (Rh³⁺), and 224.2 (Ir⁴⁺). The detector type was RACID charge injection device.

Batch and Column Adsorption Studies

Batch Study

The batch adsorption studies were carried out by weighing 0.15 g of sorbent materials into vials containing 3 mL of 0.01 M PtCl₆^{2–} and PdCl₄^{2–} solutions in 1 M HCl medium. The mixture was shaken in a mechanical shaker (120 rpm) for 1-30 min at room temperature. The solution was then filtered and the concentrations of metal ions before and after adsorption were measured by ICP-OES.

The percentage adsorption (A%) of each metal ion was determined using Eq. (1):

$$A\% = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

where C_e and C_o are the concentrations of the metal ions in the aqueous solutions after and before adsorption, respectively.

The adsorption capacity Q_e for each metal ion was calculated using Eq. (2).

$$Q_e = \frac{(C_o - C_e) \times V}{W}$$
(2)

where Co, Ce, W, and V are the initial metal concentration, equilibrium metal concentration, dry weight of adsorbent, and solution volume, respectively.

Adsorption Isotherms

The adsorption mode of metal ions on sorbent materials is an important factor to investigate. To explain the adsorption mode

the Langmuir and Freundlich isotherms (22) described by Eqs. (3) and (4), respectively, were used.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} + \frac{C_e}{bQ_m} \tag{3}$$

where Ce is the concentration of the metal ion at equilibrium (mg/L), Q_e is the amount of metal ion adsorbed per unit mass of the adsorbent (mg/g), the constant Qm is the theoretical saturation adsorption capacity of the monolayer (mg/g), and b is related to the energy of adsorption (L/mg).

$$\operatorname{Log} Q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of metal ions adsorbed per gram of sorbents, K_f is the Freundlich constant, and n (dimensionless) is the heterogeneity factor. The values of 1/n less than 1 represent a favorable adsorption (22).

Column Study

A glass column of length 10 cm, inner and tip diameters 3.5 and 1 mm, respectively, was plugged with glass wool, packed with 0.3 g of sorbent materials, and 5 mL of 0.01 M metal ion solutions was passed through the column. The column was washed with 5 mL of 1 M HCl. The adsorbed metal ions on the resins were eluted with 3% w/v of thiourea in 0.5 M of HNO₃. 0.5 mL eluate fractions were collected and concentrations of the metal ions were determined by ICP-OES. The separation factor of each of the metal ions was calculated by using the following equation:

$$S = \frac{[A]r}{[A]s} \times \frac{[B]s}{[B]r}$$
(5)

where $[]_r$ and $[]_s$ are concentrations of metal ions A and B on the resin and in the solution at equilibrium, respectively (23).

Separation of Chlorido Complexes of Pt(IV) and Pd(II)

The quantitative separation of chloride complexes of Pt(IV) and Pd(II) ions using each sorbent was studied by a dynamic column method. 0.3 g of resin was packed into the column and the desired volume of mixture of both metal ions solution was passed through the column to examine the competitive adsorption. The column was washed with 1 M HCl and then the adsorbed metal ions were eluted by using 0.5 M of NaClO₄ in 1 M HCl for platinum and 0.5 M thiourea in 1 M HCl for palladium. The concentration of metal ions in each fraction collected at every stage was determined by ICP-OES.

Separation of Chlorido Complexes of Pd, Pt, Ir, and Rh

The glass column was packed with 0.3 g of sorbent (S-TETA) and plugged with glass wool at the top and bottom.

5 mL of mixture of metal ions solution was passed through the column. The column was washed with 1 M HCl followed by stripping the adsorbed hexachloroplatinate (IV) with 0.5 M of NaClO₄ in 1 M HCl. The 0.5 mL eluate fractions were collected and concentrations of the metal ions were determined by ICP-OES.

Resin Regeneration

The regeneration of resin for several usage was observed by loading the columns containing 0.3 g of resin with 0.01M solution of chloride complexes of platinum(IV) and palladium(II). After reaching a maximum uptake, the resin was washed carefully with 1M of HCl. The adsorbed metal ions were stripped and eluted with 3% w/v of thiourea. After the elution, the resin was thoroughly cleaned with distilled water to ensure that it is ready for re-use for another second run of loading with a solution of metal ions (23). The elution efficiency was calculated by dividing the total uptake of the metal ion in the second run by that of the first run as given by the following equation:

% regeneration efficiency

$$= \frac{\text{Uptake of } M^{n\pm} \text{ in the second run by the resin}}{\text{Uptake of } M^{n\pm} \text{ in the first run by the resin}} \times 100^{(6)}$$

RESULTS AND DISCUSSION

Characterization of the Sorbents

a. Scanning Electron Microscopy (SEM)

The morphology of the unfunctionalized and functionalized silica microparticles was observed using a scanning electron microscope (SEM). The micrographs are shown in Fig. 2.

There were some changes in sizes of these microparticles after the introduction of different amine groups. The mesh sizes of the silica unfunctionalized ranges from 42-72 μ m, while the size increased on functionalization with EDA and TAEA which ranges from 39-82 and 80-112 μ m respectively. The particle sizes of sorbent materials with DETA and TETA functional groups reduced to 16–30 and 17-40 μ m, respectively.

b. Micrographs of silica microparticles

The micrographs of the unfunctionalized and functionalized sorbents shown in Fig. 3 revealed that the unfunctionalized silica changed color after the introduction of the amine groups. A light cream color was observed with S-EDA (Fig. 3b) and S-TAEA (Fig. 3e), while S-DETA (Fig 3c) gave a yellow color and a very deep yellow color was observed for S-TETA (Fig 3d). These color changes further confirmed that the sorbents were functionalized.



FIG. 2. SEM images of silica-based sorbents (a) unfunctionalized and (b-e) functionalized materials with amines EDA, DETA, TETA and TAEA respectively.



FIG. 3. Micrographs of silica-based sorbents (a) unfunctionalized and (b-e) functionalized materials with amines EDA, DETA, TETA and TAEA respectively.

TABLE 1 The single point surface area measurements for the unfunctionalized, EDA, DETA, TETA and TAEA-functionalized sorbent materials

Unfunctionalized (m^2/g)	EDA (m^2/g)	$\frac{\text{DETA}}{(\text{m}^2/\text{g})}$	TETA (m ² /g)	TAEA (m^2/g)
155.7	114.8	136.5	141.8	128.9

BET Surface Area

The surface area of the unfunctionalized and functionalized silica materials were measured by using the BET method. The results are presented in Table 1.

From the result in Table 1, it can be concluded that the surface area of the sorbent materials was reduced after functionalization with amine groups. The surface area increased in the order S-TETA > S-DETA > S-TAEA > S-EDA.

X-Ray Photoelectron Spectroscopy (XPS)

The surface chemistry with respect to expected atoms on the functionalized silica-based sorbents was studied by XPS. The N 1s peaks were observed around 398 eV which confirmed the functionalization with amines. The XPS spectra (Fig. 4) complimented the elemental analysis results showing the presence of nitrogen in the functionalized sorbent materials.

FT-IR Studies

The infra-red spectra of the unfunctionalized material, 3chloropropyltrimethoxysilane and the functionalized material as shown in Fig. 5. The spectrum of the linker for the amines to the silica particle, 3-chloropropyltrimethoxysilane, showed a strong peak at 670 cm⁻¹ which is characteristic of ν (C-Cl). This peak disappears after functionalization of the linker with amines followed by attachment onto the silica surface, and other significant peaks were observed: 1671 cm⁻¹ δ (N-H), and 1046 cm⁻¹ ν (Si-O) (24). This indicated that all the sorbent material contained an amine group after functionalization.

Batch Adsorption Studies

The effect of contact time on the adsorption of platinum and palladium chlorido species is shown in Fig. 6. The adsorption of platinum and palladium reached maximum in about 5 minutes. Only a slight increase in adsorption of the metals was obtained after 15 mins, hence 20 mins was taken as the contact time for subsequent experiments.

In order to investigate the adsorption mode of $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$ on each sorbent, the adsorption studies were carried out using the batch method and results were fitted on the Freundlich and Langmuir isotherms. The adsorption result obtained for both metals ions as the log Q_e vs log C_e for the Freundlich isotherm on S-DETA sorbent and their fit with experimental data are presented in Fig. 7. These isotherms are frequently used to describe the adsorption of metal ions during



FIG. 4. The XPS spectra of (a) EDA, (b) DETA, (c) TETA and (d) TAEA-functionalized materials.



FIG. 5. FT-IR spectra of (a) 3-chloropropyltrimethoxysilane (b) S-EDA (c) S-DETA (d) S-TETA (e) S-TAEA and (f) unfunctionalized silica.

a process of ion exchange (22) and the results are summarized in Table 2.

It is observed from the higher correlation coefficients (\mathbb{R}^2) that the Freundlich isotherm model was suitable for representation of the experimental data. This isotherm described the adsorption on heterogeneous surface of the adsorbents. From the result it was clear that the values of 1/n were less than 1 which indicated favorable adsorption.

Column (Dynamic) Studies

Single Element Studies

The sorbents performance under dynamic flow adsorption conditions was studied. The single element studies were carried out initially for the evaluation (screening) of the materials for their interactions with the anions. In 1 M HCl solutions



FIG. 6. Effect of contact time on adsorption percentage (A %) using 3 mL of 0.01 M platinum and palladium chlorido species on 0.15 g of S-DETA at room temperature.



FIG. 7. Plots of Freundlich isotherm model using 3 mL of 0.01 M \blacksquare Pt and \blacktriangle Pd on 0.15 g of S-DETA at room temperature.

there is significant perturbing power of the chloride anion to displace the metal ions chlorido species but if the interaction of the metal ion species is stronger than that of the chloride anion then it will load significantly on the solid phase. There is no approach for calculating the association constants for $[PtCl_6]^{2-1}$ and $[PdCl_4]^{2-}$ on the solid phase and hence the screening presented an easier option. Thiourea was used for the elution step, and it is well known for its affinity for precious metals due to the presence of both amine and sulfur groups. These contribute to the binding of the metal ions by complexation (25), possibly forming a cationic Pd complex $[Pd(NH_2)_2CS)_4]^{2+}$ due to the kinetic lability of [PdCl₄]²⁻ to ligand substitution reactions (26). It has been used for desorption of precious metals from loaded sorbents (27). The Pt and Pd were quantitatively desorbed using 3% w/v of thiourea in 0.5 M of HNO₃. The columns were loaded with higher metal quantities so as to allow

TABLE 2 and $PdCl^{2-}$

f.....

Frequencies parameter for adsorption of Fict_6^- and Fict_4^- on functionalized since-based incroparticles									
Isotherm	Parameters	S-EDA (Pt)	S-DETA (Pt)	S-TETA (Pt)	S-TAEA (Pt)	S-EDA (Pd)	S-DETA (Pd)	S-TETA (Pd)	S-TAEA (Pd)
Freundlich	$K_F (mg/g)$ n	9.98 1.91	10.00 1.92	10.00 2.09	9.98 1.92	9.98 1.92	9.98 1.92	9.98 1.92	10.00 1.92
Langmuir	R ² Q _m b	0.998 0.34 4.4	0.999 0.09 0.2	0.999 0.02 0.03	0.997 2.8 2.3	0.998 0.002 1.0	0.999 0.36 2.2	0.998 0.13 3.7	0.999 0.15 2.2
	\mathbb{R}^2	0.789	0.842	0.509	0.688	0.567	0.341	0.820	0.506



FIG. 8. Adsorption/elution profiles using 5 mL of 0.01 M $PtCl_6^{2-}$ and $PdCl_4^{2-}$ on 0.3 g of amine-functionalized silica-based sorbents: S-EDA, S-DETA, S-TETA and S-TAEA respectively by eluting with 3% w/v thiourea at room temperature.

for the calculation of loading capacities when the un-adsorbed metals have been washed off the column. Figure 8 represents the curves for the elution profiles of $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$ on functionalized silica-based sorbent.

Platinum and palladium were loaded on other sorbents with exception of S-TETA sorbents on which platinum came off the column during the washing step and loaded palladium was eluted with the eluting agent as shown in Fig. 8. The interaction of $[PdCl_4]^{2-}$ with TETA is suspected to be via bidentate coordination since Pd(II) in $[PdCl_4]^{2-}$ is known to be more labile to substitution compared with Pt(IV) in $[PtCl_6]^{2-}$ (28). The loading capacity for platinum and palladium on the sorbents were in the range S-TETA > S-DETA> S-TAEA > S-EDA (Table 3). The trend in loading capacity is in agreement with the BET surface areas and elemental analysis result with

respect to percentage of nitrogen, hence confirming that surface area and nitrogen content influences adsorption. The mass balance for the column adsorption of both metal ions Pt(IV) and Pd(II) on the functionalized silica materials shows that the recovery efficiency is about 95% of what was loaded into the column.

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The selectivity of S-TETA for $[PdCl_4]^{2-}$ was examined by determining the separation factor of Pt(IV) and Pd(II). A binary synthetic solution containing equimolar concentration of both metal ions was loaded into the pre-conditioned column, stripped and eluted with 3% w/v of thiourea. The separation factor of $[PdCl_4]^{2-}/[PtCl_6]^{2-}$ was 79. The selectivity of S-TETA was further investigated by the breakthrough curves represented in Fig. 9. From the curve the breakthrough volume for palladium was significantly higher (above 10 mL).

 TABLE 3

 The experimental loading capacities of functionalized Pt and Pd (mg/g) on sorbents

Metal ions	S-EDA (mg/g)	S-DETA (mg/g)	S-TETA (mg/g)	S-TAEA (mg/g)
Pt	0.24	0.40	0.00	0.29
Pd	0.14	0.16	0.25	0.15



FIG. 9. Breakthrough curves for separation of $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$ on 0.3 g of S-TETA sorbent at room temperature. Metals concentration = 0.01M each (in 5 mL) and HCl concentration = 1 M. Stripping was carried out with 0.5 M perchlorate followed by 0.5 M thiourea in 1 M HCl.

Binary Separation of Pt and Pd

The separation of a mixture of Pt(IV) and Pd(II) was carried out by taking advantage of their different stripping conditions and the results are presented in Fig. 10. The metals loaded on the resins were efficiently stripped with 0.5 M NaClO₄ in 1 M HCl for [PtCl₆]²⁻ and 0.5 M thiourea in 1 M HCl for [PdCl₄]²⁻.

The results of the selective separation of the platinum and palladium using the S-EDA sorbent revealed that both metal ions can be successfully separated by using a stripping agent that is specific to one metal chlorido species over the other. In this work NaClO₄ was used to strip $[PtCl_6]^{2-}$ from the mixture of the metal solution while thiourea in HCl medium was used to elute Pd(II) after the removal of Pt.

Separation of Pd from Pt, Ir, and Rh

A column study of the adsorption of $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$ showed the selectivity of S-TETA sorbent for $[PdCl_4]^{2-}$ as shown in the overlaid curves (Fig. 8). This study was



FIG. 10. The curves of separation of $PtCl_6^{2-}$ and $PdCl_4^{2-}$ by selective stripping of Pt with NaClO₄ and Pd with thiourea using S-EDA sorbent.



FIG. 11. The adsorption/elution profile of Pd from the mixture of Pt, Ir and Rh on 0.3 g S-TETA under 1 M HCl conditions at room temperature. 1 M HCl was used for the washing step (fractions 0–5), perchlorate in 1 M HCl for the stripping step (fractions 6–14) and then the elution step with 3% w/v thiourea (fractions 15–25).

then extended to further investigate the specificity of the S-TETA sorbent for palladium(II) by separating it from a mixture containing Pt(IV), Ir(IV), and Rh(III). The difference in adsorption behavior of these metals in HCl medium depends on the distribution of their chlorido ionic species. In the case of Ir and Rh, these metal ions came off the column at the point of starting to run and washing the loaded column with 1 M HCl along with overloaded platinum and palladium (fractions 0–5). All the Pt that was loaded came off at the stripping step (fractions 6–12) suggesting that the perchlorate effect was significant and that Pd was adsorbed in the column was quantitatively eluted with thiourea (fractions 15–24). It is clear from fractions 6–12 that the metal ions species ([PtCl₆]^{2–}, $[IrCl_5(H_2O)]^-$, $[RhCl_3(H_2O)_3]$, and $[PdCl_4]^{2-}$) that occur at 1 M HCl have some ion exchange interaction with the protonated resin. $[RhCl_3(H_2O)_3]$ had the least interaction; hence it was not adsorbed while the anionic species showed the order $[PtCl_6]^{2-} > [PdCl_4]^{2-} > [IrCl_5(H_2O)]^-$ which is the order of charge density of these anions. The truly Pd(II) specificity of S-TETA is demonstrated by the possible removal of Pd(II) through only the use of thiourea (fractions 15–24) suggesting that there is coordination of the metal ion to TETA rather than the ion exchange experienced in the earlier fractions (6–12).

Regeneration of Resin

Regeneration efficiency described by Eq. (6) also proved that the efficiency of polyamine-functionalized silica materials was retained even after repeated processes and this was determined to be 95% of the initial capacity. This further proved that the functionalized silica materials can be used several times for adsorption and separation of platinum group metals.

CONCLUSIONS

The sorbents loading capacity is directly proportional to the total exposed surface areas and also on the percentage of nitrogen in the material. The mechanism of $[PtCl_6]^{2-}$ and [PdCl₄]²⁻ binding on the sorbents followed the multilayer adsorption on heterogeneous surface of the adsorbents described by Freundlich isotherm model. The continuous column experiments indicated that separation of $[PtCl_6]^{2-}$ and [PdCl₄]²⁻ was achieved on S-EDA sorbent by selective stripping of [PtCl₆]²⁻ with 0.5 M NaClO₄ in 0.5 M HCl and Pd(II) with 0.5 M thiourea in 1 M HCl. The separation of Pd from mixture of solution containing platinum, iridium, and rhodium was achieved on sorbent S-TETA rendering it a palladium(II)specific sorbent material albeit with a low loading capacity (0.27 mg/g). It is desirable to study the underlying chemistry in the interaction of [PdCl₄]²⁻ with S-TETA but the current work suggests coordination of Pd(II) to triethylenetetramine, possibly via the bidentate coordination of the two middle nitrogens which have relatively low pK_a values for the protonated forms. The tetrachloridopalladate(II) complex is also known to readily form chelates with amines in mildly acidic chloride-rich solutions due to the kinetic lability of $[PdCl_4]^{2-}$ to ligand substitution reactions. However, this warrants a detailed investigation of this chemistry on the solid phase (S-TETA).

ACKNOWLEDGEMENTS

We would like to thank the Electron Microscopy Unit (Rhodes University) for the SEM facilities.

FUNDING

We are also grateful to the National Research Foundation (NRF) South Africa for funding.

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