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Selective sorption of palladium by thiocarbamoyl–substituted thiacalix[*n*]arene derivatives immobilized in amberlite resin: Application to leach liquors of automotive catalysts

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Manabu Yamada,[a,*] Muniyappan Rajiv Gandhi,[a] Yoshihiko Kondo,[b] Kazutoshi Haga,[c] Atsushi Shibayama[d] and Fumio Hamada[c]

p-*tert*-Butylthiacalix[4/6]arenes (**1** and **2**) and their thiocarbamoyl derivatives (**3** and **4**) were immobilized on Amberlite XAD-7 (XAD). Pd(II) adsorption from single-metal solution, simulated mixed-metal solution, and automotive catalyst leach liquor in HCl media was performed in the batch mode. The Pd(II) sorption capacity of **3** and/or **4** immobilized on XAD (**7** and **8**) was 40.2 mg/g and 60.0 mg/g, respectively. In contrast, **1** and/or **2** immobilized on XAD (**5** and **4**) had lower sorption capacity than **7** and **8**, 10.1 mg/g and 13.4 mg/g, respectively. Resins **7** and **8** selectively sorbed 99% of Pd(II) ions from automotive catalyst liquor comprising Rh, Pd, Pt, Zr, Ce, Ba, Al, La, and Y in 0.1 M HCl media. XAD and the extractant-impregnated XAD resins were characterized by FT-IR, XRD, SEM-EDAX, and WDXRF before and after Pd(II) sorption. The sorption data were fitted to Freundlich and Langmuir isotherms. Thermodynamic parameters such as ΔG^o, ΔH^o, and ΔS^o were calculated to evaluate the nature of the sorption process. Pd(II) sorption efficiency of **7** and **8** was also tested by column method. Desorption of Pd(II) ions from the loaded resins was performed using acidic thiourea, thereby enabling recycling of the resins. Thus, both resins **7** and **8** can be used for the effective separation of Pd(II) from secondary resources.

Introduction

Platinum, palladium, and rhodium are platinum group metals (PGMs) that are widely used in industry as catalysts. These metals are employed in catalytic converters to oxidize or reduce automobile exhaust emissions.[1] According to a 2010 survey, ca. 58% of Pd, 40% of Pt, and 83% of Rh, based on the world's total production, is used in the automobile catalytic converter industry.[2] The combination of three PGMs (such as Pt, Pd, and Rh) is used in three-way catalysts to reduce the emission of HC, CO, and NO_x from catalytic converters.[3a] Variation of the quantity of Pt, Pd, and Rh in catalytic converters has been evaluated, where each catalytic converter contained 1–2 g of PGMs per converter.[3b] However, the three aforementioned PGMs, mostly concentrated in specific areas such as South Africa, Canada, Russia, and North America, occur in very low quantities in primary ores, on average ~ 10 g/t. Despite their limited availability, the demand for PGMs has continued to increase because of their wide range of applications, *e.g.*, in automotive catalysts, electronic devices, and jewelry. Therefore, recycling of PGMs from waste catalysts is an important task from the perspective of economics. This recycled waste may serve as a supplementary resource to the mining of PGMs. However, mutual separation of Pd(II)/Pt(IV) is an important and difficult task because of the similar chemical properties of these species. Thiacalixarenes are composed of phenol rings linked with elemental sulfur and are ranked among the highly versatile macrocyclic species such as crown ethers, cyclodextrins, and calixarenes. Thiacalixarenes have been found to exhibit different chemical and physical properties relative to those of calixarenes. A distinct feature of thiacalixarenes is their capability for infinite intermolecular interaction, because the bridging sulfide moieties lead to strong interactions with a wide range of metal ions such as alkali, transition, and lanthanide metal ions.[4] In addition, *p*-*tert*-butylthiacalix[4/6]arenes extracted Pd(II) ions by coordination to the bridging sulfur and the two pendent phenolate oxygen atoms. In our previous study,[5] solvent extraction of Pd(II) from the acidic leach liquor of automotive catalyst solution using a chloroform solution of *p*-*tert*-butylthiacalix[4/6]arenes and their thiocarbamoyl derivatives was evaluated. The thiocarbamoyl compounds exhibited excellent Pd(II) extraction via coordination of thiocarbamoyl groups. We also evaluated Pd(II) stripping, acid durability, and reusability.[5] However, the practical use of calixarenes and thiacalixarenes in solvent extraction is still limited because of their low solubility in the diluents.[6] Calixarenes and

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[a] *Research Center for Engineering Science, Graduate School of Engineering and Resource Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan.*

[b] *Department of Life Science, Graduate School of Engineering and Resource Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan.*

[c] *Department of Applied Chemistry, Graduate School of Engineering and Resource Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan*

[d] *Faculty of International Resource Sciences, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan.*

* Corresponding author. Tel: +81 18 889 3068; fax: +81 18 889 3068.
E-mail address: myamada@gipc.akita-u.ac.jp

Electronic Supplementary Information (ESI) available: [specifications of Amberlite XAD-7 resin; chemical structure of XAD and cluster model of XAD surface; supplementary tables and figures are provided]. See DOI: 10.1039/x0xx00000x thiacalixarenes are soluble in chlorinated hydrocarbon diluents such as chloroform, dichloromethane, and dichloroethane at millimolar levels.[6] On the other hand, solid-phase separation of PGMs is simpler, more economical, nontoxic, and eco-friendly than solvent extraction.[6] Therefore, it is expected that solid-phase separation by using thiacalixarene-based extractants immobilized on polymer resin should be effective for PGM recovery. Many commercial extractants, as well as calixarene/thiacalixarene derivatives, have been used for the preparation of impregnated resins to separate various metal ions.[7-11]

Amberlite XAD-7 (XAD) resin, an acrylic-ester-resin, exhibits intriguing features such as a chemical stability, high porosity, uniform pore size, high surface area, and a non-ionic structure.[11b] The main advantage of the resin is that it possesses a continuous pore structure and a matrix classified as a macro-reticular cross-linked polymer.[12a] This resin has exhibited excellent removal capacity for biomolecules, organic compounds, plant extracts, organic pollutants, and Au(III).[12] Herein, we report the impregnation of *p-tert*-butylthiacalix[4/6]arenes and their thiocarbamoyl-modified derivatives into XAD resin and selective sorption of Pd(II) from single metal solutions and leach liquors of automotive catalysts containing nine metal ions using the immobilized species. Analysis of the sorption isotherms and thermodynamic parameters, is employed to elucidate a plausible mechanism for Pd(II) sorption by these systems. Comparison of the sorption capacities of various functionalized polymers/commercial resins for the separation of Pd(II) from aqueous solutions reported in the literature is also presented.

Experimental

Materials and methods

Amberlite XAD-7 resin, which is a porous synthetic resin, was supplied by Organo Corporation, Japan. Specifications of the resin provided by the manufacturer are summarized in the ESI Table S1. The chemical structure of XAD[12a] and a cluster model of the XAD surface[12c] are presented in the ESI Fig. S1. Stock solutions of each metal ion were prepared using $PdCl_2$ (Kanto Chemical Co., Inc.), H_2PtCl_4 (Acros Organics), $RhCl_3{\cdot}3H_2O$, $AlCl_4$, $YCl_3{\cdot}6H_2O$, $ZrCl_4$, $LaCl_3{\cdot}7H_2O$, $BaCl_2{\cdot}2H_2O$ (Wako Pure Chemical Industries, Ltd.), and $CeCl_3{\cdot}7H_2O$ (Nacalai Tesque, Inc.) in HCl solution. All other chemicals were of reagent grade and were used without further purification. Metal solutions at various concentrations were prepared by dissolving the required quantities of the respective metal salts in doubly-distilled water.

Preparation of thiacalix[*n*]arene impregnated resins

p-tert-Butylthiacalix[4]arene (**1**), *p-tert*-butylthiacalix[6]arene (**2**), 5,11,17,23,29,35-*tert*-butyl-37,38,39,40,41,42-(dimethylthiocarbamoyl)oxythiacalix[4]arene (**3**), and 5,11,17,23-tert-butyl-25,26,27,28-(dimethylthiocarbamoyl)oxythiacalix[6]arene (**4**) were synthesized according to our reported method.[5] Amberlite XAD-7 resin (XAD) was sequentially washed with doubly-distilled water, acetone, and 1 M HCl to remove unreacted monomeric material and impurities. The resin was further rinsed with doubly-distilled water and washed with chloroform. The resin was filtered and dried at 60°C in a vacuum oven to remove excess chloroform. The extractants, **1** (0.72 g, 1.0 mmol), **2** (0.54 g, 0.5 mmol), **3** (1.06 g, 1.0 mmol), and **4** (1.60 g, 1.0 mmol), were dissolved in chloroform. The chloroform solutions of the extractants were colorless and immiscible with water; the native extractants are not soluble in water. Respective 10 g samples of the conditioned resin were immersed in chloroform solutions of the extractants for 24 h. The impregnated resins were then collected by filtration. Finally, the resins were washed with chloroform and dried for several hours at 60°C in vacuo until a constant weight was obtained. The quantity of extractant immobilized in the resin was calculated based on the difference in the mass of the extractant-impregnated resin and bare XAD. The respective loadings of **1-4** in the XAD resins were 0.048, 0.025, 0.044, and 0.042 mmol/g; these impregnated resins are hereafter termed **5** (**1**-XAD), **6** (**2**-XAD), **7** (**3**-XAD), and **8** (**4**-XAD), respectively. The impregnated resins were stored in an inert atmosphere and used for the batch and column sorption studies.

Pd(II) adsorption experiments

Batch sorption experiments were conducted by placing 0.1 g of an impregnated resin into a 250 mL Erlenmeyer flask containing 100 mL of an aqueous solution of 0.1 g/L Pd(II) ions in the desired concentration of HCl. The contact time (10–270 min), HCl concentration (0.001–8.0 M), and initial concentration of Pd(II) ions (0.02–0.2 g/L) were varied for each sample. The Erlenmeyer flasks were agitated using a thermostated shaker at a speed of 140 rpm and the solution was filtered using a Avantec no. 5C filter paper. The initial concentrations of metal ions in the prepared solution and in the filtrate were determined via inductively coupled plasma atomic emission spectrometry (ICP-AES; SPS-3000; Seiko Instruments Inc.). Duplicate measurements were performed and the residual concentration values were reproducible within ±5%. The sorption capacities (SCs) were calculated as follows:

$$\boldsymbol{Sorption\ capcity\ (SC), q = [(C_0 - C_e)/\mathrm{m}] \times \mathrm{V} \quad \mathrm{mg/g}} \qquad (1)$$

$$\boldsymbol{Percentage\ metal\ sorption, S\ \% = [(C_0 - C_e)/C_o] \times 100} \qquad (2)$$

where *q* is the SC of the resin (mg metal ion/g resin), *V* is the volume of the metal ion solution (L), C_0 is the metal ion concentration before adsorption (mg/L), C_e is the metal ion concentration after adsorption (mg/L), and *m* is the weight of the resin (g). The adsorption isotherms and thermodynamics were evaluated at different initial Pd(II) concentrations (0.04, 0.06, 0.08, and 0.1 g/L) in 0.001 M HCl and at different temperatures (293, 303, and 313 K).

Adsorption of simulated single-metal ions by 7 and 8

The acid-leached automotive catalyst residue contained nine metal ions, Rh, Pd, Pt, Zr, Ce, Ba, Al, La, and Y. Hence, simulated single-metal ion sorption using Pd, Pt, Rh, Y, Zr, Ba, Al, La, and Ce was studied using single-metal solutions with concentrations of 0.1 g/L that were prepared from the corresponding chloride salts in 0.1 M HCl media. 100 mL aliquot of each single-metal ion solution was mixed with 0.1 g of **7** or **8**. The mixture was shaken at 140 rpm for 150 min. The solution was then filtered and the residual metal ion concentration was measured by ICP-AES.

Adsorption of a simulated mixed solution containing nine metals by 7 and 8

Adsorption of metals from simulated mixed solutions containing nine metals (Pd, Pt, Rh, Y, Zr, Ba, Al, La, and Ce) was carried out. A mixed solution containing Pd, Pt, Rh, Y, Zr, Ba, Al, La, and Ce ions (0.1 g/L) in 0.1 M HCl was prepared from the respective chloride salts. Because the diluted leach liquors contained 0.93 g/L Pd(II) ions, we fixed the concentration of metal ions in the mixed metal ion solution to 0.1 g/L to evaluate the Pd(II) selectivity of **7** and **8** in the presence of a high concentration of other metals. A 100 mL aliquot of the mixed solution containing the nine metals was combined with 0.1 g of **7** or **8**. The mixture was shaken at 140 rpm for 150 min. After sorption, the concentrations of the nine metal ions in the aqueous phase were measured by ICP-AES.

Characterization and chemical analysis

The extractant-impregnated resins (EIRs) and Pd(II)-sorbed resins were photographed using a NIKON D5200 digital camera to distinguish the color changes before and after the sorption experiments. FT-IR spectra were measured at 4000–600 cm^{-1} using a Thermo Fisher Scientific Nicolet iS5 spectrophotometer (attenuated total reflection method; Thermo Fisher Scientific). The FT-IR spectra were used to analyze the functional groups before and after Pd(II) sorption by the resins. X-Ray diffraction (XRD) analysis of the resins was performed using a Rigaku RINT–2200/PC system with a Cu Kα irradiation source (λ = 1.5405 Å) at 40 kV and 50 mA. The EIRs and the Pd(II)-sorbed EIRs were analyzed in continuous scan mode in the 2θ range of 10° to 80° to determine the crystalline phases. The surface morphology of the resins before and after Pd(II) sorption was studied using a Hitachi SU-70 ultra-high-resolution analytical field emission scanning electron microscope (FE-SEM). Elemental spectra were obtained during the SEM observations by using an energy dispersive X-ray analyzer (EDAX) that allows qualitative detection and localization of elements in the resin. Quantitative determination of the major and minor atomic elements in the EIRs and in the Pd(II)-sorbed EIRs was performed by using a RIGAKU ZSX Primus II wavelength dispersive X-ray fluorescence spectrometer (WDXRF) equipped with a Rh X-ray tube using 50 kV voltage and 50 mA current; SQX fundamental parameter software by EZ-scan was utilized. Computations were performed with Microcal Origin (Version 6.0) software. The goodness of fit was determined based on the regression correlation coefficient (*r*) and chi-square (χ^2) analysis.

Adsorption of PGMs from acid–leached automotive catalyst solution by 7 and 8

PGM solutions were prepared from automotive catalyst residue by treating the residue with conc. HCl (12 M) and H_2O_2 (1.0 vol.%).[13] The PGM solutions contained nine metal ions, Rh, Pd, Pt, Zr, Ce, Ba, Al, La, and Y. The solutions were diluted five-fold with water and used for the sorption study. The pH of the diluted PGM solutions was 1 (~ 0.1 M HCl). The concentrations of metal ions in the diluted solutions were determined by ICP-AES. A 0.5 g sample of **7** or **8** was mixed with 100 mL of the leached solution of automotive catalyst residue. The mixture was shaken at 140 rpm for 150 min. The concentrations of the metal ions remaining in the aqueous phase were determined by ICP-AES.

Desorption of Pd(II) ions from resin

Samples of **7** and **8** (0.5 g) were mixed with 100 mL of leached automotive catalyst solution (pH 1) and the mixture was shaken at 140 rpm for 150 min. Desorption of Pd(II) ions from metal-adsorbed **7** and **8** was performed by using mixing 0.5 g of the metal-sorbed resins with 100 mL of 0.1 M thiourea-1 M HCl solution. The mixture was shaken at 140 rpm for 150 min (20 ± 1 ^{o}C) and the concentration of Pd(II) ions in the aqueous phase after desorption was determined by ICP-AES. The percentage Pd(II) desorption was calculated using the following equation:

$$\boldsymbol{Percentage\ Pd(II)\ desorption, D}\ \% = [(\boldsymbol{C_0} - \boldsymbol{C_e})/\boldsymbol{C_o}] \times \mathbf{100} \qquad (\mathbf{3})$$

where C_0 is the weight of initially sorbed Pd(II) (mg/g) and C_e is the equilibrium concentration of Pd(II) in the resin after recovery (mg/g).

Reusability of 7 and 8

Respective samples (0.5 g) of the Pd(II) desorbed resins (washed with water and dried) were again shaken with 100 mL of automotive catalyst leach liquor for 150 min at 140 rpm. The solution was then filtered, and the concentration of Pd(II) ions in the aqueous phase was determined by ICP-AES. Five successive sorption/desorption cycles were performed to assess the reusability of the sorbent.

Results and discussion

Pd(II) sorption by XAD and extractant-impregnated resins

The sorption capacity (SC) of XAD and the EIRs for Pd(II) in 0.001 M HCl was evaluated by varying the contact time in the range of 10–270 min. Approximately 0.1 g of the resin and 100 mL of a Pd(II) solution with an initial concentration of 0.1 g/L were used for each test. Fig. 1 shows that the SCs of the EIRs for Pd(II) reached saturation after 150 min. Increasing the contact time did not lead to any further increase of the SC of the resins. The Pd(II) SC of the XAD resin was markedly low (3.8 mg/g) owing to its neutrality. On the other hand, the Pd(II) SC of the thiacalixarene-impregnated resins was notably higher. The Pd(II) SCs obtained with **5–8** were 10.1, 13.4, 40.2, and 60.0 mg/g, respectively, and were achieved with a contact time of 150 min or more. Increasing the number of sulfur atoms in the immobilized thiacalixarene derivatives **1-4** was associated with an increase in the Pd(II) SCs of **5-8**. Among the EIRs, **7** and **8** containing thiocarbamoyl groups had the highest Pd(II) SC due to the strong Pd(II) complexation ability of **3** and **4**.[5] In contrast, the resins containing **1** and **2** had a low Pd(II) SC relative to the SC of **7** and **8**.

Sorption of Pd(II) ions as a function of HCl concentration

The Pd(II) SC of the impregnated resins depends on the acid concentration. Sorption experiments were carried out by immersing 0.1 g of the EIRs in 0.1 g/L of Pd(II) in 0.001-8 M HCl solutions for 150 min. From evaluation of the contact time, it was determined that the resins require ~150 min to achieve the maximum Pd(II) sorption and hence, in this study, a contact time of 150 min was maintained. The resulting Pd(II) sorption achieved with **5-8** is summarized in Fig. 2. Maximum Pd(II) SCs of 10–3.5 mg/g and 13.4–4.2 mg/g were respectively obtained with resins **5** and **6** in 0.001–

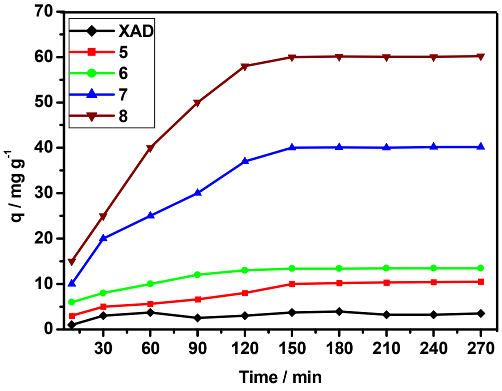


Fig. 1 Effect of contact time on the Pd(II) SCs of the resins. Pd(II) = 0.1 g/L; [HCl] = 0.001 M; Resin = 0.1 g

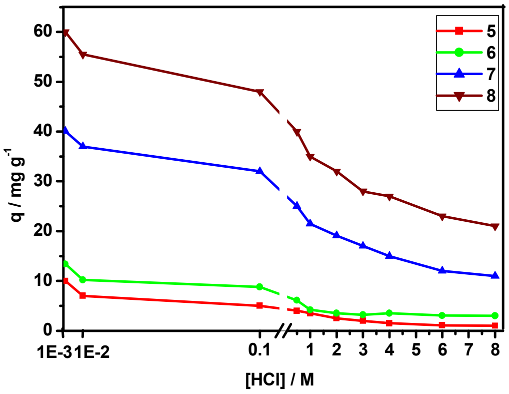


Fig. 2 Sorption of Pd(II) ions as a function of [HCl] by impregnated resins. Pd(II) = 0.1 g/L; [HCl] = 0.001-8.0 M; Time = 150 min; Resin = 0.1 g

1.0 M HCl. Much lower SCs were obtained with the use of 2.0-8.0 M HCl because deprotonation of the phenolic groups was inhibited by the HCl medium. Thus, the extractants could not form complexes with Pd(II) via the bridging sulfur. These results indicated that **5** and **6** were not suitable for the sorption of Pd(II) in acidic media.[5,14] In contrast, resins **7** and **8**, which contain thiocarbamoyl moieties, had higher Pd(II) SCs than **5** and **6** even in very highly acidic media.[5] The Pd(II) SC of **7** was in the range of 60-35 mg/g in 0.001-2.0 M HCl and 32-21 mg/g in 4.0-8.0 M HCl, while the Pd(II) SC of **8** was in the range of 40-21.5 mg/g in 0.001-1.0 M HCl and 19-11 mg/g in 2.0-8.0 M HCl. Therefore, the Pd(II) SC of resin **8** was much higher than that of **7**, owing to the difference in the number of thiocarbamoyl groups. The optimum HCl concentration for maximizing the Pd(II) sorption of **5-8** ranged from 0.001-1.0 M. The observed decline of the Pd(II) SCs in the case of the impregnated resins in 2.0-8.0 M HCl is attributed to the high concentration of Cl^- ions in the medium.[14] High concentration of Cl^- ions inhibits the complex formation of Pd(II) with **7-8**.

Effect of Pd(II) concentration on impregnated resins

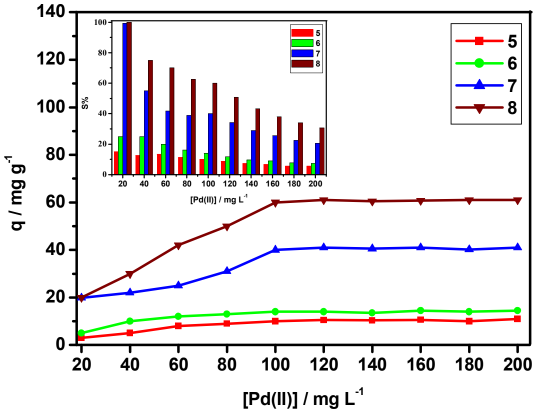


Fig. 3 Effect of Pd(II) ions concentration on impregnated resins. Pd(II) = 0.02 -0.2 g/L; [HCl] = 0.001 M; Time = 150 min; Resin = 0.1 g

The Pd(II)-loading capacity of **5–8** (0.1 g) was investigated by varying the initial Pd(II) concentration from 0.02 to 0.20 g/L using a fixed contact time of 150 min using 0.001 M HCl as the medium. Pd(II) uptake by the EIRs increased as the initial concentration increased up to 0.1 g/L; thereafter, there was no further increase. The maximum uptake of Pd(II) by **5–8** when the initial concentration of Pd(II) of 0.1 g/L was 10.0, 14.0, 40.0, and 61.0 mg/g, respectively (Fig. 3). The S (%) values of **5–8** decreased with increasing initial Pd(II) concentration (inset of Fig. 3).

Notably, the Pd(II) SC of **7** and **8** was much higher than that of **5** and **6** when 0.1 g of the resins was used. Hence, further experiments were carried out only for **7** and **8**.

Sorption of Pd(II), Pt(IV), Rh(III), and other metals from respective single-metal solutions

Single-metal extraction of all nine metal ions (Rh, Pd, Pt, Zr, Ce, Ba, Al, La, and Y) present in the automotive catalyst was evaluated using 0.1 g of **7** and **8** in HCl media (0.1 M). The Pd(II) SC obtained with resins **7** and **8** was very high (32 and 48 mg/g, respectively) compared with the SC of these resins for the other metal ions studied (Fig. 4), which were all <2.0 mg/g. These results clearly indicate that **7** and **8** have a remarkably high affinity for Pd(II) ions and were found to uptake very large amounts of Pd(II) ions.

Sorption of Pd(II), Pt(IV), Rh(III), and other metals from mixed-metal solutions

In order to study the selectivity of **7** and **8** for Pd(II), the sorption of Pd(II) in the presence of competing metal ions was evaluated by using a mixed-metal solution derived from actual leached automotive catalyst solution. Resins **7** and **8** adsorbed large quantities of Pd(II) ions from the mixed-metal ion solution, as shown in Fig. 5. A Pd(II) sorption capacity of 33.5 mg/g was obtained with **8**, while that obtained with **7** was 21.0 mg/g when 0.1 M HCl was used as the medium for mixed-metal ion solutions. There was a slight decrease of the Pd(II) SCs of these resins in mixed-metal solution (cf. Fig. 4). The decline in the Pd(II) SCs may

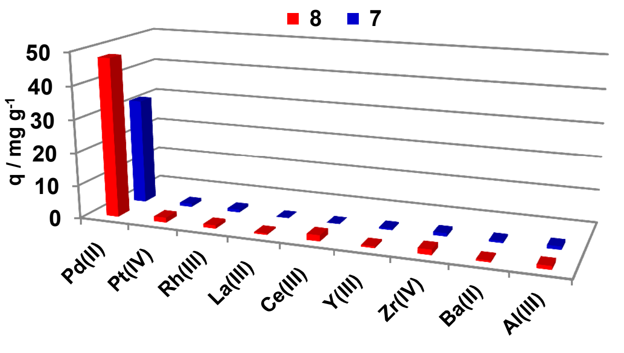


Fig. 4 Sorption of Pd(II), Pt(IV), Rh(III), and other metals from single-metal solutions by **7** and **8**. Single metal ion = 0.1 g/L; [HCl] = 0.1 M; Time = 150 min; Resin = 0.1 g

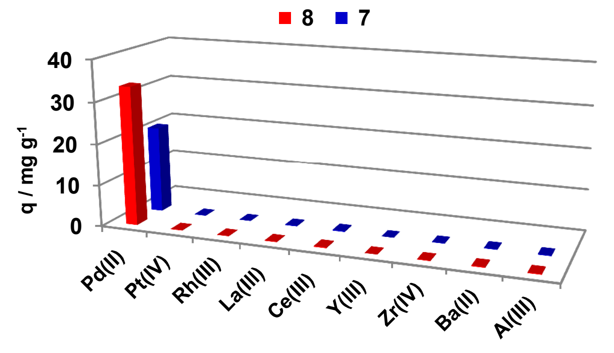


Fig. 5 Sorption of Pd(II), Pt(IV), Rh(III), and other metals from mixed-metal solutions by **7** and **8**. Mixed metal ion = 0.1 g/L ; [HCl] = 0.1 M; Time = 150 min; Resin = 0.1 g

be due to inhibition of interactions between Pd(II) ions and the resins in the presence of high concentrations of other metals in the mixed solution. The sorption of other metal ions was found to be <2.0 mg/g. As mentioned above, resins **7** and **8** exhibited clear selectivity towards Pd(II) sorption in 0.1 M HCl medium .[5]

Characterization of impregnated resins and Pd(II) adsorbed impregnated resins

FT-IR spectra of resins. FT-IR spectra of XAD, **8**, and Pd(II)-sorbed **8** were recorded (ESI Fig. S2). XAD is an aliphatic cross-linked polymer that contains an acrylic ester group. The ester group present in the XAD resin gave rise to three strong infrared bands at 1724, 1257, and 1140 cm^{-1} corresponding to C=O stretching, C-C-O stretching, and O-C-C stretching, respectively.[12b,f,g] The peak at 2965 cm^{-1} is derived from stretching vibrations of the C–H bonds in the resin.[12b] In addition, the peaks at 1463 and 1387 cm^{-1} are due to deformation of the C–H bonds of the CH_3 groups.[12f] After impregnation of **4** with XAD, a new, weak peak corresponding to C=S appeared at 1540 cm^{-1}, indicating the successful impregnation of **4** into the resin matrix.[5] After Pd(II) sorption, the weak peak corresponding to C=S disappeared, possibly due to interaction of Pd(II) ions with the C=S group, whereas there was no significant change in the intensity of the other peaks. It is difficult to identify the Pd peaks using FT-IR because their characteristic absorptions occur at 600-200 cm^{-1}, which is mostly outside of the evaluated IR region (4000-400 cm^{-1}).

XRD analysis. X-Ray power diffraction patterns of XAD, **8**, and Pd(II)-sorbed **8** are presented in ESI Fig. S3. The XRD spectrum of the XAD resin was indicative of an amorphous nature and a weak shoulder was present around 2θ = 10°. The XRD profile of **8** was also indicative of an amorphous nature. After impregnation of **4** into XAD, there was a slight change in the XRD spectrum with an increase in the intensity of the peak near the 2θ = 10°. The change in the XRD spectrum before and after impregnation with **4** can be ascribed to the interaction of **4** with XAD.[7b] The XRD spectra of Pd(II)-sorbed **8** showed new small peaks at 2θ = 31.8 ° and 45.8 ° with retention of the amorphous nature of the resin; thus the interaction of palladium with **8** was confirmed. [7b,14f]

Digital images and SEM-EDAX studies. The adsorption of Pd(II) on the resins was clearly identified from digital photographs of the impregnated resins and Pd(II)-treated impregnated resins (Fig. 6 (a-h)). Digital images of **5**-**8** are presented in Fig. 6 (a,c,e,g), demonstrating that all of the resins impregnated with **5**-**8** were colorless. Fig. 6 (b,c,e,g) shows digital images of Pd(II)-sorbet **5**-**8**. After Pd(II) sorption, the color of **5** and **6** changed from white to light brown to dark brown.[9b] The Pd(II) sorption capacity of **5** was far less than that of **6** based on the visually observed light brown color versus the deep, dark brown color of **6** after Pd(II) sorption. After Pd(II) sorption, resins **7** and **8** color change from white to black.[9b] The Pd(II) sorption capacity of both resins was very high based on their intense black color. SEM images of resin **8** and Pd(II)-sorbed resin **8** are shown in Fig. 7a and b. A clear difference between the bare resin and the Pd(II)-loaded resin was apparent.

The image presented in Fig. 7b shows many glowing metallic spots on the surface of the resin. From the two images in Figs. 7a and b, it can be concluded that Pd(II) species were adsorbed on the surface of **8**. This conclusion was also supported by EDAX analysis. Figs. 7c and d show the EDAX spectra and quantitative elemental compositions of **8** and Pd(II)-sorbed **8**. The spectra show peaks corresponding to C Kα (0.22 keV), N Kα (0.39 keV), O Kα (0.52 keV), and S Kα (3.60 keV). The EDAX spectrum of Pd(II)-sorbed **8** shows new peaks corresponding to Pd Lα at 2.8 keV and Cl Kα at 2.6 keV; the percentage of Pd(II) was found to be 1.56 wt.%. The quantitative composition of other elements present in the resin and their percentages are also presented in the respective figures. The data clearly indicate sorption of Pd ions into the matrix of **8**.

WDXRF analysis. Quantitative determination of the major and minor atomic elements in the surface of the resin was performed via WDXRF. The presence of C, O, S, and N was confirmed from the WDXRF spectra of **8**. In contrast, new peaks of Pd and Cl were observed in the WDXRF spectra of Pd(II)-sorbed **8**. ESI Figs. S4a and b show the respective C Kα (2θ = 32.7°) spectra of **8** before and after Pd(II) sorption. There was no change in the intensity of the C Kα peak of resin **8** before and after Pd(II) sorption. The intensities of the N Kα (2θ = 46.9°) and O Kα (2θ = 34.6°) peaks of **8** before and after Pd(II) sorption are shown in ESI Figs. S5 and S6. A minor peak split was observed in the same region. The intensity of the S Kα (2θ = 110.8°) peaks of Pd(II)-sorbed **8** compared to that of **8**, as shown

Fig. 6 (a,c,e,g,) Digital photographs of the **5**, **6**, **7**, and **8** respectively and (b,d,f,h) Pd(II) treated**5**, **6**, **7**, and **8** respectively.

in ESI Fig. S7. Interestingly, two new peaks were observed in the profile of Pd(II)-treated **8** (Fig. 8) where the peaks with high intensity correspond to Pd Kα (2θ = 16.7^o) and Pd Kβ (2θ = 14.8^o). An intense Cl Kα (2θ = 92.8^o) peak was observed in the profile of Pd(II)-treated **8** (Fig. 9). Thus, sorption of Pd(II) by **8** exerted an effect on the intensity of the strong, new peaks corresponding to Pd, Cl, and S. The results suggest that Pd(II) sorption by **8** occurs via complex formation through the sulfur moiety of the thiocarbamoyl group present in **8**. The WDXRD studies also showed that 1.2 wt.% of Pd(II) was present in Pd-sorbed **8**. Although the WDXRD data for **8** could not be interpreted directly to elucidate the sorption mechanism in solution, it is clear that the sorbed resin contains a substantial portion of Pd(II).

Sorption isotherms. To quantify the sorption capacity of **7** and **8**, the removal of Pd(II) ions from aqueous solution was evaluated and the sorption data were evaluated by employing the two most commonly used isotherm models, namely the Freundlich and Langmuir isotherms.

Freundlich isotherm. The linear form of the Freundlich isotherms is represented by the following equation: [15a]

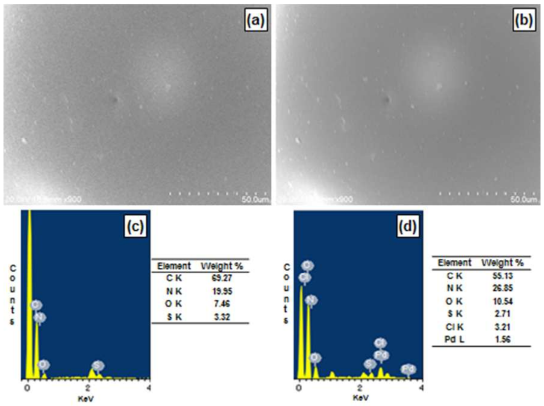
$$\log q_e = \log k_F + \frac{1}{n}\log C_e \qquad (4)$$

where q_e is the amount of Pd(II) adsorbed per unit mass of the resin (mg/g), C_e is the equilibrium concentration of Pd(II) in solution (mg/L), k_F is a measure of the adsorption capacity, and $1/n$ is the adsorption intensity. The corresponding Freundlich isotherms for **7** and **8** are presented in Fig. 10a and b. The values of the Freundlich isotherm constants for both resins were calculated from the linear plots of log q_e vs. log C_e as listed in Table 1. The plot of log q_e vs. log C_e was linear as indicated by the high r values, which indicates the applicability of the Freundlich isotherm. The n values between 1 and 10 indicated that Pd(II) adsorption was a favorable process.[15b] The k_F values decreased with increasing temperature, indicating that Pd(II) sorption by the impregnated resins is an exothermic process.

Langmuir isotherm. The Langmuir isotherm model is represented by the following equation: [15c]

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad (5)$$

where Q^0 is the amount of adsorbate at complete monolayer coverage (mg/g), from which the maximum sorption capacity of the



Element	Weight %
C K	69.27
N K	19.95
O K	7.46
S K	3.32

Element	Weight %
C K	55.13
N K	26.85
O K	10.54
S K	2.71
Cl K	3.21
Pd L	1.56

Fig. 7 SEM images of (a) **8** and (b) Pd(II)-sorbed **8**. EDAX spectra of resins (c) **8**, (d) Pd(II)-sorbed **8**.

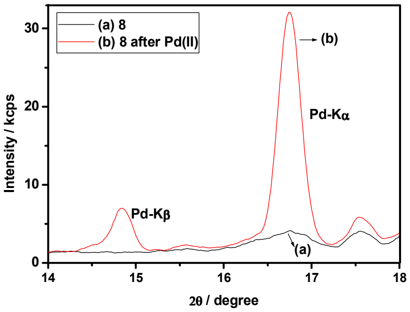


Fig. 8 WDXRF spectra of (a-b) Pd Kα Kß for **8** before and after Pd(II) sorption.

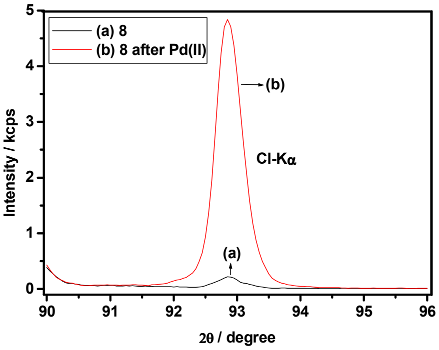


Fig. 9 WDXRF spectra of (a-b) Cl Kα for **8** before and after Pd(II) sorption.

sorbent can be derived, and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption.[15d] The respective Langmuir isotherms for **8** and **7** are shown in Figs. 11(a) and (b). The Langmuir isotherm constants, Q^0 and b, for both resins were respectively calculated from the slope and intercept of the linear plots of C_e/q_e vs. C_e (Table 1). The *r* values of the linear plots of C_e/q_e vs. C_e were high, which indicates the applicability of the Langmuir isotherm. The values of Q^0 and b decreased with increasing temperature, indicating that Pd(II) sorption by both resins was exothermic. To evaluate the applicability of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter, R_L.[15e]

$$R_L = {}^{1}\!/_{1 + bC_0} \qquad (6)$$

where b is the Langmuir isotherm constant and C_o is the initial concentration of Pd(II) (mg/L). The R_L values, being between 0 and 1, indicate favorable adsorption of Pd(II) at for all of the temperatures studied (Table 1).

Chi-square analysis. To identify a suitable isotherm model for Pd(II) sorption by the impregnated resins, chi-square (χ^2) analysis was carried out.[15f] The equivalent mathematical statement is:

$$\chi^2 = \frac{(q_{e-}q_{e,m})^2}{q_{e,m}} \qquad (7)$$

where $q_{e,m}$ is the equilibrium capacity obtained from the model calculations (mg/g), and q_e is the experimental data for the equilibrium capacity (mg/g). If the data from the model are similar to the experimental data, χ^2 will be small; while if they differ, χ^2 will be larger. The results of the χ^2 analysis are presented in Table 1. The lower χ^2 values of the Langmuir isotherm compared with the Freundlich isotherm suggest the applicability of the former as the better fitting model for the sorption of Pd(II) by **7** and **8**.

Thermodynamic treatment of the sorption process. The thermodynamic parameters associated with adsorption (*i.e.*, the standard free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o)) were calculated as follows: the free energy of the sorption process, considering the sorption equilibrium coefficient $K_{0,}$ is given by the equation:

$$\Delta G^o = -\mathbf{R}T\ln K_0 \qquad (8)$$

where ΔG^o is the standard free energy of sorption (kJ/mol), *T* is the temperature (K), and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). The sorption distribution coefficient K_o, was determined from the slope of the plot of ln (q_e/C_e) vs. C_e, at different temperatures and by extrapolating to zero C_e, according to the method suggested by Khan and Singh (1987).[15g] The sorption distribution coefficient may be expressed in terms of ΔH^o and ΔS^o as a function of temperature:

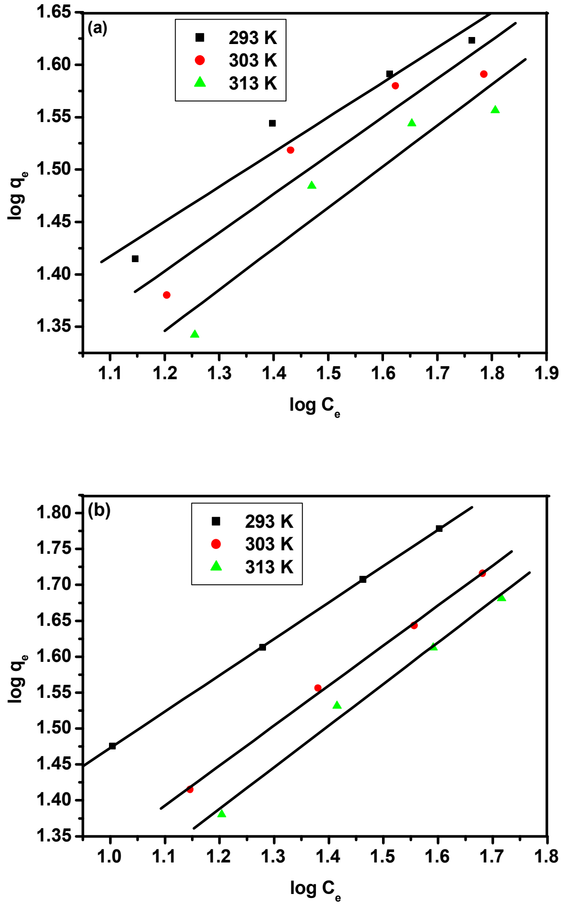


Fig. 10 Freundlich isotherm of (a) **7** and (b) **8**.

$$\ln K_0 = \frac{\Delta S^o}{\mathbf{R}} - \frac{\Delta H^o}{\mathbf{R}T} \qquad (9)$$

where ΔH^o is the standard enthalpy change (kJ/mol) and ΔS^o is the standard entropy change (kJ/mol K). The values of ΔH^o and ΔS^o can be obtained from the slope and intercept of the plot of ln K_o vs. 1/*T* (ESI Fig. S8 (a-b)). The calculated thermodynamic parameters for the impregnated resins are shown in ESI Table S2. A negative ΔG^o indicates that Pd(II) sorption by the resins is spontaneous. The negative ΔH^o indicates that the sorption process is exothermic. The negative value of ΔS^o indicates decreased randomness at the solid/solution interface during Pd(II) sorption. Increasing the temperature does not favor the Pd(II) sorption process based on Le Chatelier's equilibrium law.

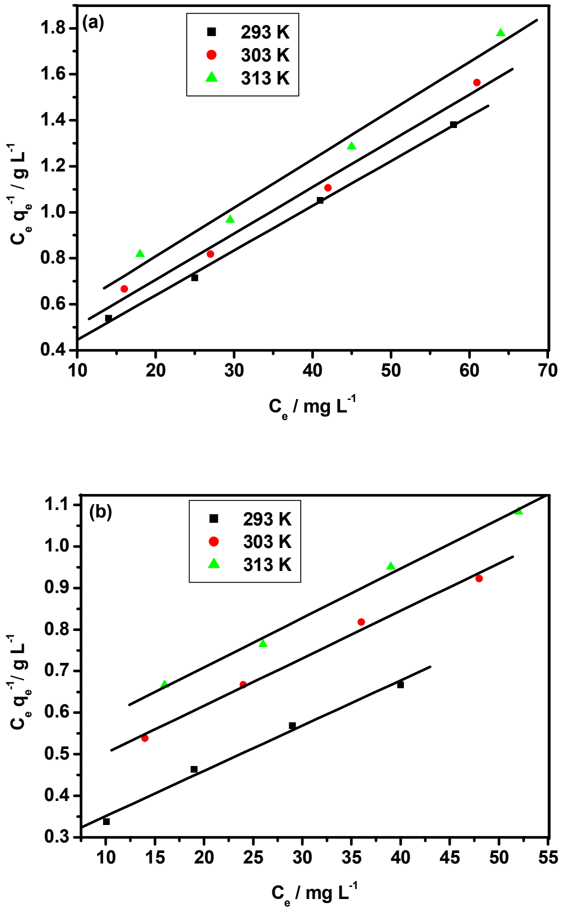


Fig. 11 Langmuir isotherm of (a) **7** and (b) **8**.

Metal ion sorption from automotive catalyst solution. Metal ions were leached from an automotive catalyst by treating the catalyst with HCl (11.6 M) and H_2O_2 (1 vol%) at 65 °C for 3 h.[13] Ratio of solid to liquid (pulp density) during the leaching was 500g/L. The resultant leached solution, which contained nine metal ions (Rh, Pd, Pt, Zr, Ce, Ba, Al, La, and Y), was diluted with distilled water to 5 times its original volume; the pH was then adjusted to 1.0. The concentrations of metal ions in the diluted solution were determined by ICP-AES as listed in Table 2. The automotive catalyst leached solution contains a very high concentration of metal ions that precipitate above pH 1.5; therefore, the pH was fixed at 1.0 (~0.1 M HCl) for the sorption studies. The impregnated resins (0.5 g) were added to the solution (100 mL) and the mixture was then shaken at 140 rpm for 150 min. The concentration of metal ions remaining in the solution was determined by ICP-AES. Resins **8** and **7** were the most effective for Pd(II) sorption (E% > 99 (q = 18 mg/g), indicating selective extraction of Pd(II) from the PGM solution by **8** and **7** (Fig. 12). The other metal ions in the acid-leached automotive catalyst solution was adsorbed <2.6%. Thus, it is concluded that **8** and **7** can selectively separate Pd(II) ions from acid-leached automotive catalyst solutions containing other metal ions because the thiocarbamoyl functional groups selectively remove Pd(II) ions as reported in a previous article.[5]

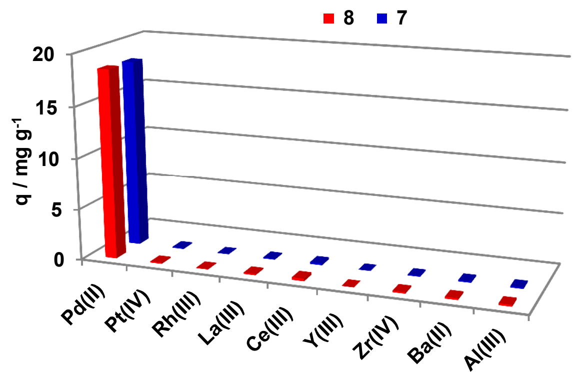


Fig. 12.Sorption of Pd(II) from a PGM solution containing nine metal ions (Al, Ba, Ce, La, Pd, Pt, Rh, Y, and Zr) by **7** and **8**. [HCl] = 0.1 M; Time = 150 min; Resin = 0.5 g

Pd(II) uptake using the fix-bed columns from automotive catalyst solution.

On a laboratory scale, continuous flow adsorption experiments were conducted by using Alltech® Maxi-clean™ Standard C18 polypropylene cartridge, which is the solid phase extraction (SPE) cartridge of 1.0 cm width and 1.0 cm length. 0.1 g of resin **7** and **8** are filled in the cartridge and 20 µm polyethylene frits are placed in each end of the resin bed. At the bottom of the column, 50 times diluted leached automotive catalyst solution in 0.1 M HCl (Pd(II): 9.2 mg/L; Pt(IV): 5.4 mg/L; Rh(III): 3.71 mg/L; La(III): 8.65 mg/L; Ce(III): 60.8 mg/L: Zr(IV): 2.5 mg/L; Y(III): 0.38 mg/L; Ba(II): 28.9 mg/L, and Al(III): 32 mg/L) was pumped through the packed column whose height is 0.5 cm, at flow rates of 0.1 mL/min, using a micro tube pump set (Front Lab FP 100, As one corporation, Japan). Samples were collected from the top exit of the column at regular time intervals and analyzed for residual metal concentrations using ICP-AES. The Pd(II) adsorption capacity for **7** and **8** through column sorption was calculated by the following Eq.

$$q_e = \int_0^V \frac{(C_0 - C)dV}{m} \quad mg/g \qquad (10)$$

where q_e is the Pd adsorbed (mg/g), C_0 is the input Pd concentration (mg/L), C is the output Pd concentration (mg/L), V is the volume of solution required to reach the saturation or breakthrough point (L) and m is the mass of impregnated resin (g).

The adsorbent exhaustion rate (AER) was calculated as follows:

$$\begin{aligned}&\textbf{Adsorbent exhaustion rate}\\&\quad = \textbf{mass of the resin } (\boldsymbol{g})\\&\quad / \textbf{Volume of solution treated } (\boldsymbol{L}) \qquad (\mathbf{11})\end{aligned}$$

For both the resins, almost 99.9% sorption of Pd from the automotive catalyst solution at initial fractions was obtained, while fixed breakthrough for Pd(II) concentration of 0.1 mg/L in the output automotive catalyst solution occurred at about 60 mL for resin **8** and 30 mL for resin **7** (Fig. 13). The Pd(II) sorption capacity (q_e) of the resin **8** at breakthrough volume was calculated to be 0.78

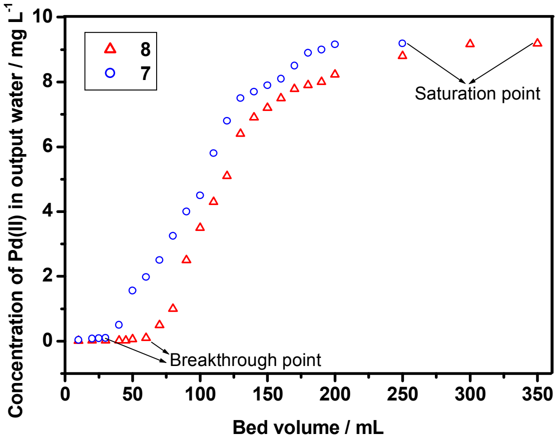


Fig. 13 Breakthrough curves of Pd(II) adsorption by **7**-**8**. Resin = 0.1 g; Bed height = 0.5 cm; flow rate = 0.1 mL/min;[Pd(II)] in automotive catalyst solution = 9.2 mg/L

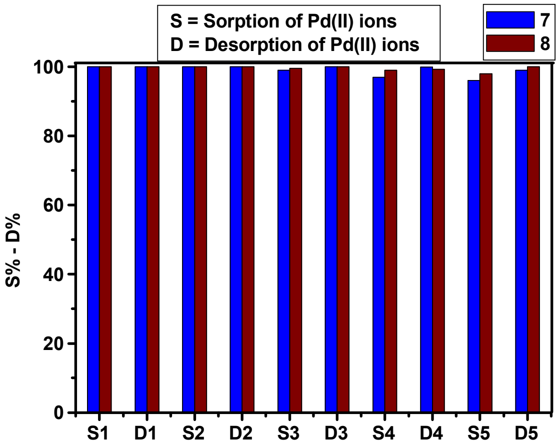


Fig. 14 Sorption and desorption cycle of **7** and **8**. Resin= 0.5 g; Time = 150 min; [HCl] = 0.1 M; [Pd(II)] in automotive catalyst solution = 92.8 mg/L

mg/g and at saturation point was 0.34 mg/g (influent automotive catalyst solution volume was 350 mL). The Pd(II) sorption capacity (q_e) of the resin **7** at breakthrough volume was calculated to be 0.68 mg/g and at saturation point was 0.30 mg/g (influent automotive catalyst solution volume was 250 mL). The other metals in the influent automotive catalyst solution were not adsorbed on the resins. The concentration of the other metal ion in the influent and effluent automotive catalyst solution almost remains the same. The S% of the all other metals ions in the automotive catalyst solution were < 0.1%. The resins **8** and **7** showed more than 99.0 % Pd (II) sorption up to 45 mL and 30 mL respectively (ESI Fig. S9). The percentage of sorption (S%) of Pd(II) decreased gradually above 30 mL and 45 mL for **7** and **8**, respectively. The decrease in percentage of Pd(II) adsorption could be attributed to the decreased resin–Pd(II) interaction. The Pd(II) adsorption is quantitative at an optimized flow rate of 0.1 mL/min, which ensures effective contact between the Pd(II) and the impregnated resins. The performance of resin is expressed in terms of the rate at which the resin bed gets exhausted; the rate is calculated from the ratio of the mass of resin to volume maximum automotive catalyst solution treated. In the present study, with 0.1 g of the resin, at 9.2 mg/L Pd(II), the exhaustion rate of the resin **7** and **8** is 3.3 g/L and 2.2 g/L, respectively. From the foregoing discussion, a lower exhaustion value of AER signifies the good performance of the resin in the bed. Hence, the resin **7** and **8** can be used on an industrial scale, with an increase in the amount of the resin in the column, large volume of automotive catalyst solution would be enhanced and high amount of Pd(II) can be recovered from automotive catalyst solution.

Sorption and desorption cycle. Sorption experiments were conducted by mixing **7** and **8** (0.5 g) with 100 mL of leached automotive catalyst solution (pH 1); the mixture was shaken at 140 rpm for 150 min. The percentage Pd(II) sorption and the sorption capacity of the resin were calculated. Recovery of Pd(II) ions from Pd(II)-sorbed **7** and **8** was then performed. A 0.5 g sample of the resins after sorption of the acid-leached liquor was mixed with 0.1 M thiourea in 1 M HCl (100 mL). The mixture was shaken at 140 rpm for 150 min and the concentration of Pd(II) ions in the aqueous phase after recovery was determined by ICP-AES. The equilibrium concentration of Pd(II) ions in the resins after recovery (mg/g) was calculated. The Pd(II) desorbed resin was subsequently washed with water in order to remove any thiourea. Sorption and desorption with the resins was repeated for 4 more cycles; the percentage sorption and desorption for successive cycles is presented in Fig. 14. In the first and second sorption and desorption cycles, S% and D% were 100 % for **7** and **8**. At the end of the fifth sorption and desorption cycle, S% and D% were 96-98% for both resins. Resins **7** and **8** exhibited very high Pd(II) sorption capacity and efficient and complete Pd(II) desorption with the use of 0.1 M thiourea in 1 M HCl. The high S% and D% for Pd(II) ions exhibited by resins **7** and **8** leads to facile regeneration and reuse of the resins. Pd(II) could be selectively removed from the acid-leached automotive catalyst by solid-phase separation using **7** and **8**.

Mechanism of Pd(II) sorption by impregnated resins.

Liquid-liquid extraction of Pd(II) from acid-leached automotive catalyst solution using chloroform solutions of **3** and **4** was previously assessed.[5] A mechanism for Pd(II) removal using extractants **3** and **4**, stripping of the Pd(II) ions, and the acid durability of **3** and **4**, as well as their reusability have been discussed in our previous report.[5] Based on our previous studies[5] as well as FT-IR and WDXRF results (ESI Fig. S2 and S7) showed that **5** and **6** could adsorb Pd(II) ions by coordination to the bridging sulfur and the two pendent phenolate oxygen atoms. In contrast, resins **7** and **8** could form complex Pd(II) ions through the thiocarbamoyl groups.[5] The proposed major Pd(II) ion–sorption mechanism of **7** and **8** is shown in Fig. 15. ESI Table S3 shows a comparison of the SC of a few polymers reported in the literature for Pd(II) separation from aqueous solutions for comparison with the performance of the impregnated resins.[16-19] The prepared resins exhibited superior Pd(II) SC relative to the congeners reported in the literature, which confirms their selectivity towards Pd(II).

Table 1 Freundlich and Langmuir isotherm parameters of **7** and **8**.

Resin	Temp. (K)	Freundlich				Langmuir				
		n	k_F (mg/g) $(L/mg)^{1/n}$	*r*	χ^2	Q^o (mg/g)	b (L/g)	R_L	*r*	χ^2
7	293	0.322	11.246	0.973	0.107	51.55	0.077	0.114	0.999	0.012
	303	0.367	9.162	0.950	0.123	49.75	0.066	0.131	0.994	0.048
	313	0.391	7.516	0.949	0.118	47.39	0.054	0.179	0.991	0.050
8	293	1.973	9.240	0.999	3.86E–3	91.74	0.045	0.181	0.994	2.18E–3
	303	1.795	6.011	0.999	3.66E–3	87.72	0.029	0.253	0.966	2.20E–3
	313	1.721	4.920	0.995	1.96E–2	84.10	0.024	0.286	0.997	9.54E–3

Table 2 Concentrations of metal ions in the leached solution of automotive catalyst after five-time dilution.

Metal ions	$[M]_{aq,init}$ (mg/L)
Al(III)	320.98
Y(III)	3.80
Zr(IV)	25.68
Rh(III)	37.12
Pd(II)	92.85
Ba(II)	289.33
La(III)	86.56
Ce(III)	608.78
Pt(IV)	54.26

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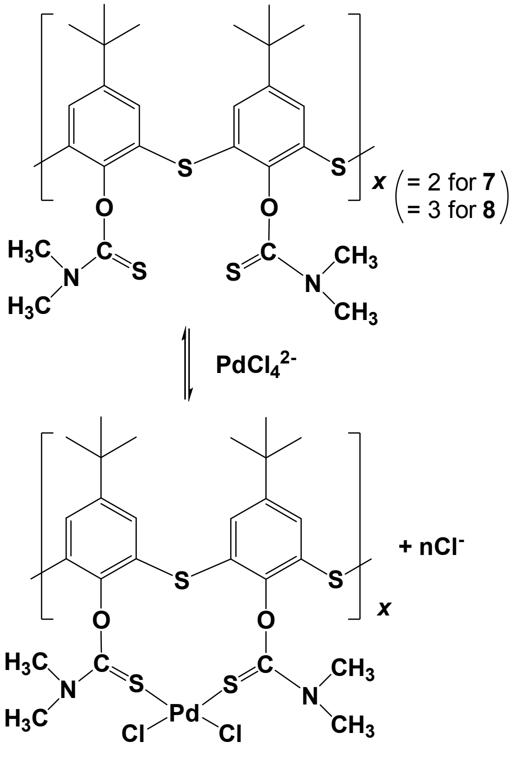

Fig. 15 Proposed Pd(II) ion−sorption mechanism by extractants in the resin **7** and **8**.

Conclusions

Comparison of thiocarbamoyl derivatives **7** and **8** of *p-tert*-butylthiacalix[4/6]arenes immobilized on XAD showed that resin **8** was more effective for Pd(II) sorption than resin **7**, which, in turn was more effective than the parent *p-tert*-butylthiacalix[4/6]arenes immobilized on XAD (resins **5**/**6**). Introduction of the thiocarbamoyl groups resulted in enhanced Pd(II) sorption due to the high Pd(II) complexation ability of these groups. Maximal Pd(II) sorption with the developed resins required a contact time of 150 min or greater. Pd(II) sorption by the resins was strongly influenced by the HCl medium and decreased slightly in the presence of Rh, Pd, Pt, Zr, Ce, Ba, Al, La, and Y. The Pd(II) SC of **8** was found to be 60–35 mg/g in 0.001–2.0 M HCl and 32–21 mg/g in 2.0–8.0 M HCl. Pd(II) SC of **7** was 40.1–21.5 mg/g in 0.001–1.0 M HCl and 19.9–11 mg/g in 2.0–8.0 M HCl. Resins **5** and **6** exhibited much lower Pd(II) affinity due to inhibition of deprotonation of the phenolic groups by the acid, which precluded formation of complexes with Pd(II) through the bridging sulfur. The Langmuir isotherm model could be applied to the sorption of Pd(II) ions by **7** and **8**, where the process was exothermic in both cases. Resin 7 and 8 adsorbed 99.9% of Pd(II) ions from an acid-leached automotive catalyst solution. In the fixed column study, **7** and **8** showed good performances and their exhaustion rate was found to be 3.3 g/L and 2.2 g/L, respectively. The desorption (D%) for Pd(II) ions from the resin was exceeded 96% when a mixture of 0.1 M thiourea solution with 1 M HCl solution was used as a stripping agent. Resins **7** and **8** retained high SC even after five sorption cycles (S% < 97%). From these promising results, we can conclude that resins 7 and 8 have the potential for application as new adsorbents for the sorption and selective separation of Pd(II) ions from leach liquors of automotive catalysts.

Acknowledgements

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Notes and references

1 (a) M. Saternus and A. Fornalczyk, *Metalurgija*, 2013, **52**, 267; (b) S. Ravichandran, R. Venkatkarthick, A. Sankari, S. Vasudevan, D. Jonas Davidson and G. Sozhan, *Energy*, 2014, 68, 148; (c) R. Venkatkarthick, S. Elamathi, D. Sangeetha, R. Balaji, B. Suresh Kannan, S. Vasudevan, D. Jonas Davidson, G. Sozhan and S. Ravichandran, *J. Electroanal. Chem.,* 2013, **697**, 1.

2 A. Fornalczyk, *J. Achiev. Mater. Manuf. Eng*., 2012, **55**, 864.

3 (a) A. Fornalczyk and M. Saternus, *Metalurgija*, 2009, **48**, 133; (b) G. Kolliopoulos, E. Balomenos, I. Giannopoulou, I. Yakoumis and D. Panias, *Open Access Libr. J.*, 2014, **1**, e736; (c) C. Hagelüken, *Platinum Met. Rev.,* 2012, **56**, 29.

4 (a) R. Kumar, Y. O. Lee, V. Bhalla, M. Kumar and J. S. Kim, *Chem. Soc. Rev.*, 2014, **43**, 4824; (b) Y. K. Agrawal and J. P. Pancholi, *Indian J. Chem. A*, 2007, **46A**, 1373; (c) N. Morohashi, F. Narumi, N. Iki, T. Hattori and S. Miyano, *Chem. Rev.*, 2006, **106**, 5291.

5 (a) M. Rajiv Gandhi, M. Yamada, Y. Kondo, R. Sato and F. Hamada, *Ind. Eng. Chem. Res.*, 2014, **53**, 2559; (b) M. Rajiv Gandhi, M. Yamada, Y. Kondo, A. Shibayama and F. Hamada, *Hydrometallurgy*, 2015, **151**, 133.

6 (a) T. Oshima, R. Saisho, K. Ohe, Y. Baba and K. Ohto, *React. Funct. Polym.*, 2009, **69**, 105; (b) B. B. Adhikari, M. Kanemitsu, H. Kawakita, Jumina and K. Ohto, *Chem. Eng. J.* 2011, **172**, 341; (c) B. B. Adhikari, N. Hashiguchi, K. Ohto, H. Kawakita and K. Inoue, *J. Incl. Phenom. Macrocycl. Chem.*, 2009, **65**, 121; (d) B. B. Adhikari, M. Gurung, H. Kawakita and K. Ohto, *Chem. Eng. Sci.*, 2012, **78**, 144.

7 (a) S. Sharma and N. Rajesh, *Chem. Eng. J.*, 2014, **241**, 112; (b) A. S. K. Kumar, S. Sharma, R. S. Reddy, M. Barathi and N. Rajesh, *Int. J. Biol. Macromol*., 2015, **72**, 633.

8 (a) T. Vincent, A. Parodi and E. Guibal, *React. Funct. Polym.*, 2008, **68**, 1159; (b) T. Vincent, A. Parodi and E. Guibal, *Sep. Purif. Technol.*, 2008, **62**, 470; (c) K. Campos, T. Vincent, P.

Bunio, A. Trochimczuk and E. Guibal, *Solvent Extr. Ion Exch.*, 2008, **26**, 570; (d) K. Campos, R. Domingo, T. Vincent, M. Ruiz, A. M. Sastre and E. Guibal, *Water Res.*, 2008, **42**, 4019; (e) E. Guibal, K. C. Gavilan, P. Bunio, T. Vincent and A. Trochimczuk, *Sep. Sci. Technol.*, 2008, **43**, 2406; (f) E. Guibal, A. Figuerola Pinol, M. Ruiz, T. Vincent, C. Jouannin and A. M. Sastre, *Sep. Sci. Technol.*, 2010, **45**, 1935; (g) E. Guibal and T. Vincent, *Sep. Sci. Technol.*, 2006, **41**, 2533.

9 (a) R. Navarro, E. Garcia, I. Saucedo and E. Guibal, *Sep. Sci. Tech.*, 2012, **47**, 2199; b) R. Navarro, I. Saucedo, C. Gonzalez and E. Guibal, *Chem. Eng. J.*, 2012, **185–186**, 226; (c) R. Navarro, Ruiz, I. Saucedo and E. Guibal, *Sep. Purif. Tech.*, 2014, **135**, 268; (d) V. Gallardo, R. Navarro, I. Saucedo, M. Avila and E. Guibal, *Sep. Sci. Technol.*, 2008, **43**, 2434. (e) R. Navarro, I. Saucedo, M. A. Lira and E. Guibal, *Sep. Sci. Technol.*, 2010, **45**, 1950; (f) A. Arias, I. Saucedo, R, Navarro, V. Gallardo, M. Martinez and E. Guibal, *React. Funct. Polym.*, 2011, **71**, 1050; (g) R. Navarro, V. Gallardo, I. Saucedo and E. Guibal, *Hydrometallurgy*, 2009, **98**, 257.

10 (a) S. D. Alexandratos, S. Natesan, *Ind. Eng. Chem. Res.*, 2000, **39**, 3998; (b) S. Hutchinson, G. A. Kearney, E. Horne, B. Lynch, J. D. Glennon, M. A. Mckervey and S. J. Harris, *Anal. Chim. Acta,* 1994, **291**, 269; (c) X. Hu, Y. Li, Y. Wang, X. Li, H. Li, X. Liu and P. Zhang, *Desalination*, 2010, **259**, 76; (d) H. Matsumiya, S. Yasuno, N. Iki and S. Miyano, *J. Chromatogr. A*, 2005, **1090**, 197; (e) N. Iki, T. Fujimoto, T. Shindo, K. Koyama and S. Miyano, *Chem. Lett.*, 1999, 777.

11 (a) T. Oshima, R. Saisho, K. Ohe, Y. Baba and K. Ohto, *Solv. Extr. Res. Dev. Jpn.*, 2006, **13**, 123; (b) T. Oshima, R. Saisho, K. Ohe, Y. Baba and K. Ohto, *React. Funct. Polym.*, 2009, **69**, 105; (c) K. Ohto, S. Inoue, N. Eguchi, T. Shinohara and K. Inoue, *Sep. Sci. Technol.*, 2002, **37**, 1943; (d) K. Ohto, Y. Senba, N. Eguchi, T. Shinohara and K. Inoue, *Solv. Extr. Res. Dev. Jpn.*, 1999, **6**, 101; (e) N. Hashiguchi, M. Tanaka, K. Ohto, H. Kawakita and K. Inoue, *Solv. Extr. Res. Dev. Jpn.*, 2008, **15**, 99; (f) T. Nakamura, K. Ohto and K. Inoue, *Ars Separatoria Acta*, 2006, **4**, 27.

12 (a) AMBERLITE™ XAD7HP – Product Data Sheet, The Dow Chemical Company, *Form No. 177–03082–0313, pp.1–5*. http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08d2/0901b803808d2eff.pdf?filepath=liquidseps/pdfs/noreg/177-03082.pdf&fromPage=GetDoc (28th April 2015); (b) M. D. Saikia, *Colloids Surf. A: Physicochem. Eng. Asp.*, 2008, **315**, 196; (c) M. D. Saikia and N. N. Dutta, *Colloids Surf. A: Physicochem. Eng. Asp.*, 2006, **280**, 163; (d) F. Xiao, K. J. Davidsavor, S. Park, M. Nakayama and B. R. Phillips, *J. Colloid Interface Sci.*, 2012, **368**, 505; (e) P. Gogoi, M. D. Saikia, N. N. Dutta and P. G. Rao, *Biochem. Eng. J.* 2010, **52**, 144; (f) J. R. Domínguez, T. González, P. Palo and E. M. Cuerda–Correa, *Desalination*, 2011, **269**, 231; (g) N. V. Nguyen, J. Lee, S. Kim, M. K. Jha, K. Chung and J. Jeong, *Gold Bulletin*, 2010, **43**, 200.

13 *S.* Harjanto, Y. Cao, A. Shibayama, I. Naitoh, T. Nanami, K. Kasahara, Y. Okumura, K. Liu and T. Fujita, *Mater. Trans.*, 2006, **47**, 129.

14 (a) V. G. Torgov, G. A. Kostin, V. T. Mashukov, T. M. Korda, A. B. Drapailo, O. V. Kas'yan and V. I. Kal'chenko, *Russ. J. Inorg. Chem.*, 2008, **53**, 1809; (b) V. G. Torgov, T .V. Us, T. M. Korda, G. A. Kostin and V. I. Kal'chenko, *Russ. J. Inorg. Chem.*, 2012, **57**, 1621; (c) F. L. Bernardis, R. A. Grant and D. C. Sherrington, *React. Funct. Polym.*, 2005, **65**, 205; (d) H. Narita, M. Tanaka, K. Morisaku and T. Abe, *Chem. Lett.*, 2004, **33**, 1144; (e) H. Narita, M. Tanaka and K. Morisaku, *Miner. Eng.*, 2008, **21**, 483; (f) G. Mishra, D. Singh and P. K. Yadawa, *Platinum Metals Rev.*, 2013, **57**, 186.

15 (a) H .M. F. Freundlich, *Z. Phys. Chem.*, 1906, **57A**, 385. (b) M. V. Dinu, E. S. Dragan and A. W. Trochimczuk, *Desalination*, 2009, **249**, 374; (c) I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2221; (d) S. Vasudevan and J. Lakshmi, *RSC Adv.*, 2012, **2**, 5234–5242; (e) T. W. Weber and R. K. Chakravorti, *J. Am. Inst. Chem. Eng.*, 1974, **20**, 228; (f) M. Rajiv Gandhi and S. Meenakshi, J. Hazard. Mater, 2012, **203–204**, 29; (g) A. A. Khan and R. P. Singh, *Colloids Surf.*, 1987, **24**, 33.

16 (a) S. Shen, T. Pan, X. Liu, L. Yuan, Y. Zhang, J. Wang and Z. Guo, *J. Colloid Interface Sci.,* 2010, **345**, 12; (b) E. Birinci, M. Gülfen and A. O. Aydın, *Hydrometallurgy*, 2009, **95**, 15; (c) M. Iglesias, E. Antico and V. Salvado, *Anal. Chim. Acta*, 1999, **381**, 61; (d) C. Ni, C. Yi and Z. Feng, *J. Appl. Polym. Sci.*, 2001, **82**, 3127; (e) J. M. Sanchez, M. Hidalgo and V. Salvado, *React. Funct. Polym.*, 2001, **46**, 283.

17 (a) Z. Hubicki, M. Leszczyńska, B. Łodyga and A. Łodyga, *Desalination*, 2007, **207**, 80; (b) A. Kałedkowski and A. W. Trochimczuk, *React. Funct. Polym.*, 2006, **66**, 957; (c) G. V. Myasoedova, I. I. Antokol'skaya and S. B. Savvin, *Talanta*, 1985, **32**, 1105; (d) D. Shihua, T. Wanxiong and H. Yunhua, *Acta Polym. Sin.*, 1990, **2**, 142; (e) E. Antico, A. Masana, V. Salvado, M. Hidalgo and M. Valiente, *Anal. Chim. Acta*, 1994, **296**, 325.

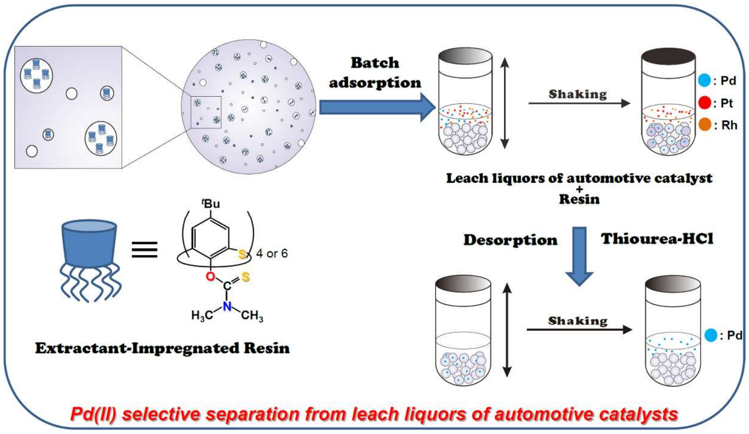
18 (a) M. Grote and A. Kettrup, *Anal. Chim. Acta*, 1985, **172**, 223; (b) S. Zhang, Q. Pu, P. Liu, Q. Sun and Z. Su, *Anal. Chim. Acta*, 2002, **452**, 223; (c) A. Das, A. K. Das and C. Sinha, *Talanta*, 1998, **48**, 1013; (d) A. Wołowicz and Z. Hubicki, *Hydrometallurgy*, 2009, **98**, 206; (e) N. Muslu and M. Gülfen, *J. Appl. Polym. Sci.*, 2011, **120**, 3316.

19 (a) C. Paduraru, D. Bilba, I. Sarghie and L. Tofan, *J. Serb. Chem. Soc.*, 2005, **70**, 1205; (b) J. M. Sánchez, M. Hidalgo and V. Salvadó, *Solvent Extr. Ion Exch.*, 2004, **22**, 285; (c) X. Chang, X. Luo, G. Zhan and Z. Su, *Talanta*, 1992, **39**, 937; (d) O. Todorova, E. Ivanova, A. Terebenina, N. Jordanov, K. Dimitrova and G. Borisov, *Talanta*, 1989, **36**, 817.

Graphical Abstract

Selective sorption of palladium by thiocarbamoyl–substituted thiacalix[*n*]arene derivatives immobilized in amberlite resin: Application to leach liquors of automotive catalysts

Manabu Yamada,* Muniyappan Rajiv Gandhi, Yoshihiko Kondo, Kazutoshi Haga, Atsushi Shibayama and Fumio Hamada



Pd(II) selective separation from leach liquors of automotive catalysts

Thiocarbamoyl-substituted thiacalix[*n*]arene derivatives immobilized on amberlite resins have the potential for application as new adsorbents for selective separation of Pd(II) ions from leach liquors of automotive catalysts.