



Highly selective recovery of palladium by a new silica-based adsorbent functionalized with macrocyclic ligand

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ABSTRACT

A new kind of silica-based adsorbent with high selectivity and efficient adsorption for palladium ion (Pd(II)) was synthesized in this study. A macrocyclic polyether isomer was modified for incorporation to the silica matrix as a ligand to realize the complexation between Pd(II) and the adsorbent. The adsorption of Pd(II) in HNO₃ media was evaluated by both batch and column operations. Influences including acidity, contact time, initial metal concentration and elution conditions were detailed. From a practical viewpoint, the functionalized adsorbent was employed for the recovery of Pd(II) from the simulated high level liquid waste (HLLW) containing a large amount of interferences. Superior selectivity to Pd(II) as well as a recovery rate higher than 90% was obtained. A mechanism concerning the formation of complex ion-pair was proposed for the description of the Pd(II)-binding process. The macrocyclic ligand functionalized silica adsorbent possesses potential for the recovery of the palladium resource in radioactive liquid waste.

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1. Introduction

As an important member of platinum group metals (PGMs), palladium is of great value in modern industry due to its favorable physical and chemical properties, such as high melting point, corrosion resistance and extraordinary catalytic ability [1,2]. In recent years, the rapid development of catalytic systems for petrochemical industry and automotive exhaust has led an increasing consumption of the precious metal. The gap between supply and demand is becoming more and more overt because of the limited palladium source in terrestrial crust with low availability. Meanwhile, from an environmental point of view, the release and accumulation of palladium in environment as a new pollutant may cause adverse health effects to human beings (e.g. eye irritations, asthma, rhinoconjunctivitis, skin problems, etc.) [3–5]. Therefore, the research on the efficient separation and recovery of palladium is in high demand.

Nowadays, it has been widely accepted that palladium recovery from industrial waste such as spent catalyst and electronic devices is valuable, and much efforts have been made to reach the goal [6–9]. However, the palladium resource present in radioactive waste stream still seems to be lack of enough concern [10,11]. According to a previous report, around 11 kg fission-generated palladium is estimated in every metric ton of the spent fuel of fast reactor, which could significantly cover the amount obtained naturally

[12,13]. Furthermore, as the volume of the accumulated high level liquid waste (HLLW) is constantly increasing worldwide, the recovery of palladium from radioactive waste stream will be considerable in economic benefit. Nevertheless, it must be admitted that, owing to the complexity of the HLLW circumstance and overlapping properties between palladium and other interfering metals, separation of palladium still faces enormous challenge [11].

In general, precious metal recycling techniques are categorized as pyro- and hydrometallurgical processes. The latter gains more popularity for easy controllability over the other one [14]. In coordination with the hydrometallurgical process, many methods including ion exchange, solvent extraction, electro-deposition, membrane separation and adsorption have been developed. Among which, adsorption has been extensively applied due to high enrichment factor, fast kinetics, minimal organic diluents utilization, and less waste accumulation [15]. Besides, the most appealing aspect of adsorption lies in the vast choice of adsorbents with wide possibilities of functionalization, making them capable for palladium ion (Pd(II)) recycling in varieties of wastewater systems. Typical cases are usually developed by using chelating resins [16,17], chemically-modified activated carbon [18,19], nanotubes [20], biomass [21–24] or functionalized silica gel [25–30] as adsorption materials. However, up to now, most of the separation protocols still suffer from a low efficiency and/or a poor selectivity. Adsorbents with selective recognition to Pd(II) have been rarely reported in the literatures [31], let alone those specialized for Pd(II) enrichment in HLLW system which contains a great many of interferences.

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The marriage between adsorption material and supramolecular chemistry has provided a boost to researches on novel adsorbents for selective metal separation lately [32–34]. Macrocyclic ligands such as crown ether, calixarene and cyclodextrin were incorporated into certain substrates (e.g. polymeric resin, silica gel, supported liquid membrane, etc.), and selective recognition towards metal ions was realized based on host–guest interaction [35–41]. Unlike binding of hard alkali metal cations, the complexation between macrocyclic ligands containing hard oxygen donors and the soft palladium ion is atypical. Talanova et al. reported a kind of divinylbenzene copolymer bearing dibenzo-18-crown-6 ligand, which showed highly efficient sorption of Pd(II) from aqueous K_2PdCl_4 solution [42]. Also, Fontàs et al. prepared a solid phase extraction support with high affinity for Pd(II) by using thiaca-lix[4]arene derivative [43]. For these cases, the hole-size fitting concept in traditional supramolecular chemistry is unconvincing, while ion-pair complex mechanism has been proposed as a seemingly reasonable explanation [44]. Overall, much more effort still needs to be made for either preparation of new functionalized adsorbents with selective Pd(II)-separation or the probing of the recognition mechanism.

In this study, we presented a novel example of macrocyclic ligand functionalized silica adsorbent which had efficient adsorption and excellent selectivity towards Pd(II) in HNO_3 media and simulated HLLW. For preparation of the adsorbent, a macrocyclic polyether isomer *cis*-di(aminocyclohexyl)-18-crown-6 was incorporated into silica matrix via a co-condensation synthetic method. The adsorption of Pd(II) in HNO_3 solution was carried out by both batch and column operations. Influences including kinetics, acidity, initial metal concentration, phase ratio, and elution condition were investigated. From a practical point of view, selective recovery of Pd(II) from simulated HLLW of a light water reactor (LWR) was performed. Mechanism about the complexation between the macrocyclic ligand and Pd(II) was discussed, and cycle use of the adsorption material was evaluated.

2. Experimental

2.1. Chemicals

Macrocyclic polyether *cis*-di(aminocyclohexyl)-18-crown-6 was synthesized according to Deetz's work [45], and molecular structure was confirmed by 1H and ^{13}C NMR spectra. Tetraethoxysilane (TEOS, 98%), di-*n*-butyltin dilaurate (DBTL, 95%) and 3-chloropropyltriethoxysilane (CPTES, 97%) were purchased from Aldrich. Deionized water with resistivity $>18 M\Omega cm$ was obtained from a Milli-Q water purification system. Stock solution of Pd(II) (92 g/L) were purchased from General Research Institute for Non-ferrous Metals. Before use, the stock solutions were further diluted by HNO_3 with different concentration. The acidity was calibrated by titration. The analytical grade chemicals, such as potassium iodide, tetrahydrofuran, and other reagents were commercially obtained and used as received without further purification.

2.2. Characterization

Nitrogen adsorption measurement of the functionalized organosilica adsorbent was carried out on a NOVA 3200e Surface Area and Pore Size Analyzer. Samples were pretreated at $140^\circ C$ under vacuum for at least 2 h before the nitrogen adsorption experiments. Surface areas were calculated based on the Brunauer-Emmett-Teller (BET) method. 1H NMR spectra were recorded by a JOEL JNM-ECA600 NMR spectrometer. ^{29}Si and ^{13}C solid-state NMR spectra were obtained with a Bruker AV300 Spectrometer with the cross-polarization/magic-angle spinning (CP/

MAS) technique. FT-IR spectra (4000 – $400 cm^{-1}$) were recorded by Nicolet Nexus 470 FT-IR in KBr matrix. X-ray photoelectron spectroscopy (XPS) measurement was performed using a PHI-5300 ESCA instrument. Elemental analysis of C, H and N was performed on Elementar Vario EL III. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (RF power supply: 1.15 kW; wavelength of element: Pd(II) 363.470 nm, Thermo Jarrel Ash mod. IRIS Advantage) and Atomic Absorption Spectroscopy (HITACHI Z-2000) were used for concentration measurement of Pd(II). The micro-morphology of the adsorbent particles was recorded by FEI Quanta 200 environmental scanning electron microscopy (ESEM). For column experiment, an YL-110 peristaltic pump and a PTFE (polytetrafluoroethylene) column ($50 mm \times 7.0 mm$ i.d.) were used.

2.3. Synthesis of functionalized silica adsorbent

2.3.1. 4,4'-Bis((3-(triethoxysilyl)propyl)amino)dicyclohexyl-18-crown-6 [1]

Cis-di(aminocyclohexyl)-18-crown-6 (4.02 g, 10 mmol) was dissolved in 250 mL tetrahydrofuran (THF), followed by the addition of 3.45 g potassium carbonate (25 mmol) and 3.32 g potassium iodide (20 mmol). Under nitrogen protection and stirring, 4.80 g 3-chloropropyltriethoxysilane (CPTES) (20 mmol) was dropwise injected. After 5 h reflux, the solid salt was separated by filtration. A brown oily product was obtained after removing the solvent of the filtrate. The product was purified via a procedure similar to that reported by Dubois et al. [37]. The final product was obtained with a yield of 47%. 1H NMR (300 MHz, $CDCl_3$): δ 3.79–3.70 (*q*, 12H), 3.67–3.54 (*m*, 16H), 3.08 (*m*, 4H), 2.69 (*m*, 6H), 1.95–1.86 (*m*, 4H), 1.60–1.52 (*m*, 8H), 1.40–1.22 (*m*, 4H), 1.19 (*t*, 18H), 0.74 (*t*, 4H). IR (KBr) (ν, cm^{-1}): 3328.6, 2985.6, 2922.8, 2857.5, 1452.3, 1354.1, 1291.6, 1220.3. ESI MS: $[M + Na]^+$ 834.20 (calc. value for $[C_{38}H_{78}N_{12}O_{12}Si_2 + Na]^+$ 833.50).

2.3.2. Functionalized silica adsorbent

Co-condensation method was used to prepare the functionalized silica adsorbent. The silanized monomer [1] (7.5 mmol) and tetraethoxysilane (TEOS) (2.5 mmol) were dissolved in quantitative anhydrous ethanol with total concentration of 1 mol/L. Under mild agitation, a stoichiometric amount of water was slowly added with a syringe, followed by 2 wt.% di-*n*-butyltin dilaurate (DBTL) as catalyst. Then, the mixture was further stirred for 10 min. Homogeneous solution was obtained and set for 3 days at ambient temperature for gelation. The product was granulated, followed by thermal treatment at $120^\circ C$ under vacuum for 8 h. The catalyst and the unreacted monomers were washed off with hot acetone. Finally, the particles were collected and dried in $60^\circ C$ vacuum oven for 24 h. Solid state ^{13}C CP-MAS NMR (300 MHz, ppm): 77.5, 71.0, 60.3, 54.1, 47.9, 26.4, 23.0, 17.6, 10.5. Solid state ^{29}Si MAS NMR (300 MHz, ppm): $-57.7, -67.5, -102.2, -110.2$. IR (KBr) (ν, cm^{-1}): 3385.5, 2929.7, 2863.2, 1465.1, 1347.4, 1101.6, 789.2, 689.8.

2.4. Pd(II) recovery by batch method

The recovery of Pd(II) in aqueous HNO_3 solutions and simulated HLLW was carried out by batch operation. In a typical process, 0.02 g functionalized organosilica adsorbent was mixed with HNO_3 solution containing about $5.0 \times 10^{-3} mol/L$ Pd(II). The acidity of the solution varied from 0.1 to 6 mol/L, and phase ratio was chosen as 0.01 g/1 mL. With vigorous agitation in $25^\circ C$ thermostat for 1 h, the aqueous phase was separated with 0.45 μm micro-pore filter. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was employed to determine the residual amount of the Pd(II) in the solution. The adsorption capacity q_t

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